1975

Denitrification of a synthetic waste with a submerged filter

Dominic Joseph Grana

Department:

DENITRIFICATION OF A SYNTHETIC WASTE WITH A SUBMERGED FILTER

BY

DOMINIC JOSEPH GRANA, 1950-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CIVIL ENGINEERING

1975

Approved by

Donald E. Mockrill (Advisor) J. Charles Jennett

L. R. Cuthbertson

ABSTRACT

The facultative anaerobic submerged filter is a plug flow, packed bed, column type reactor in which the facultative microorganisms responsible for nitrate reduction are attached to the filter media. The objective of this study was to evaluate filter performance and the kinetic equations of the process under variable conditions of flow rate, nitrate nitrogen concentration, and organic loading.

Two 0.5 cu ft (14.25 l) laboratory filters were operated for 144 days at 35°C using a synthetic waste as the substrate. Filter media consisted of smooth quartzite stone, 1 to 1.5 in. (2.54-3.82 cm) in diameter. Each filter had a porosity of 0.47 and a liquid volume of 0.22 cu ft (6.25 l).

By varying the nitrate nitrogen concentration from 3.5 to 70 mg/l and the detention time from 1 to 4 hr, a range of nitrate loadings from 9 to 735 g NO_3-N/cu m/day was achieved. Filter performance was determined by monitoring nitrate nitrogen, COD, and suspended solids.

The facultative submerged filter was found to be an effective method for denitrification of high nitrate content wastes. Nitrate removals were consistently higher than 90 percent, averaging 97 percent. COD removals were also consistently, high averaging 87 percent.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to his advisor, Dr. Donald Modesitt, for his continued interest, counsel, and understanding during this investigation. He also wishes to express his gratitude to Dr. J. Charles Jennett and Dr. Raymond Cuthbertson for their help during the revision of the manuscript.

The author wishes to thank all of his fellow graduate students and professors, whose comments and suggestions in one way or another contributed to this study. Special thanks are expressed to Michael G. Hardie and Jeanne Sickman for their timely assistance in this study, and Dr. Sotirios G. Grigoropoulos for his assistance in obtaining an Environmental Protection Agency Traineeship.

This study was supported in part by Professional Training Grant No. T-900121-02&03 from the Office of Water Programs, Environmental Protection Agency.

Finally, the author wishes to thank his wife, Rosemary, for her patience and understanding during this study.

TABLE OF CONTENTS

Page

Page

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

The forms of nitrogen which are most prevalent in waste waters are ammonia and nitrate nitrogen. There are several reasons for eliminating nitrogen from agricultural drainage or treatment plant discharges. These reasons include the oxygen demand exerted on a stream by ammonia as it is biologically oxidized from NH_3 to NO_3; the reduced effectiveness of chlorine for disinfection as a result of ammonia demand; fish kills which may occur when NH_3 is discharged to streams; the accelerated eutrophication of lakes and ponds caused by algal blooms when sufficient plant nutrients, including nitrogenous substrates, are present; and the increasing salinity of surface waters when contaminated by agricultural discharges high in dissolved solids. (1)

In recent years state and federal discharge limitations have addressed the problem of ammonia in wastewater effluents. In many cases a highly nitrified effluent is being produced and discharged. In some instances the problem of nitrate nitrogen is also being addressed relative to agricultural subsurface drainage in California (2), (3), some industrial applications such as the explosives industry or in water reclamation projects. (4), (5)

Both biological reduction and ion exchange have been utilized for denitrification. The recent successes in the treatment of low strength soluble organic wastes

by anaerobic processes (6), (7) prompted study into the application of anaerobic or facultative systems for removal of nitrates from highly nitrified effluents.

In order to capitalize on the basic operating parameters of any anaerobic system, namely low rate of cellular synthesis and long retention times, several new processes have been developed and applied including anaerobic activated sludge and other similar biological contact processes (See Figure 1). A drawback to these processes is that in most cases solids recycle is necessary to overcome the low rate of cellular synthesis. (8), (9) Several researchers (6), (7), (10) have studied the possibilities of using an anaerobic filter to take advantage of the solids retention characteristics of such a unit.

The organisms necessary to convert nitrate nitrogen into less offensive gaseous nitrogen, are facultative anaerobes. Using the principles of an anaerobic filter, that is, high solids retention time, no solids recycle, intimate contact of the waste stream with the large concentration of biological solids attached to the filter media and entrapped in the void spaces, and short hydraulic retention times, these organisms can be utilized to reduce nitrate nitrogen to nitrogen gas in a plug flow, completely submerged, rock filled, upflow reactor.

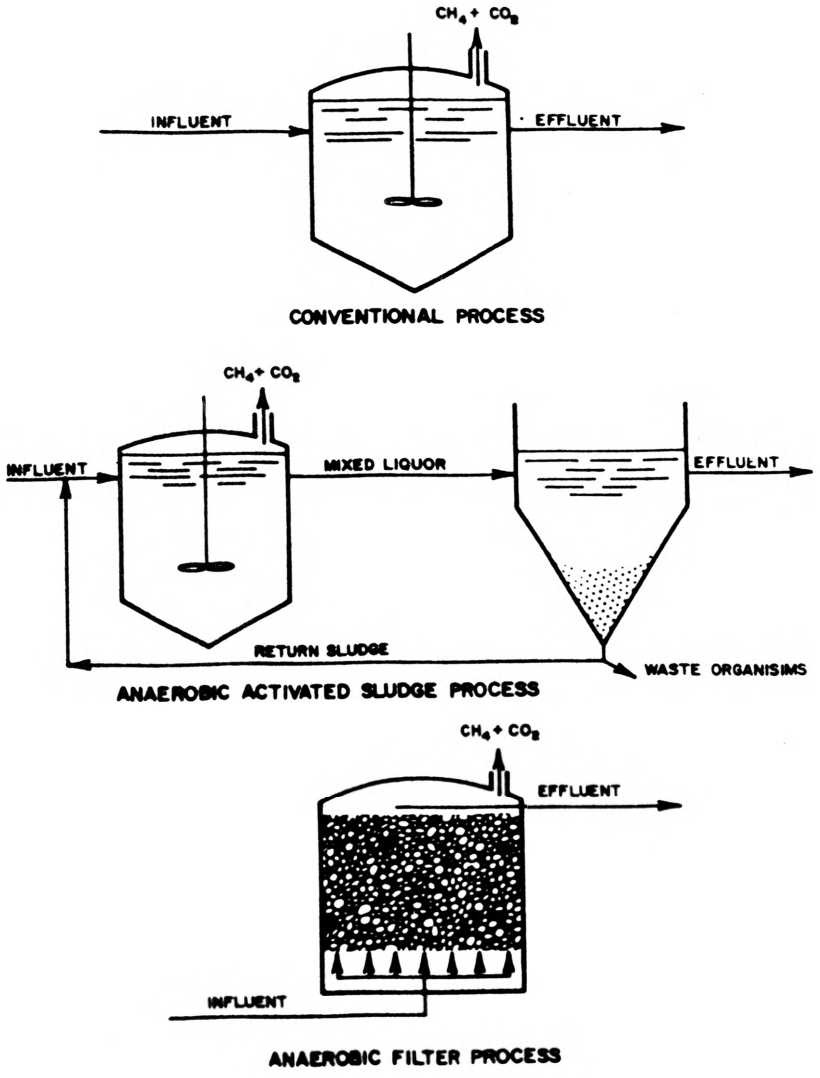


FIGURE 1. SCHEMATIC DIAGRAM OF THREE ANAEROBIC WASTE TREATMENT PROCESSES, AFTER YOUNG (6)

A. PURPOSE

It was the purpose of this investigation to:

1. Apply a synthetic waste to a submerged filter to evaluate filter performance for various hydraulic and substrate loading conditions in order to determine operational parameters;
2. Subject the filter to quantitative substrate shock loading conditions in order to determine their effect on filter performance, and;
3. Evaluate the kinetic equations for denitrification as they apply to the submerged filter.

B. SCOPE

In order to achieve the proposed objectives, a laboratory investigation was performed using 2 model submerged filters to treat the synthetic waste under controlled conditions. During the course of the study the treatment efficiency was measured as hydraulic and substrate loading rates were changed to evaluate their importance as well as the effects of shock loadings.

So that filter performance could be evaluated, parameters such as nitrate nitrogen, chemical oxygen demand (COD), pH, alkalinity, dissolved oxygen (D.O.), suspended solids (S.S.), nitrogen and nitrite nitrogen were monitored.

II. LITERATURE REVIEW

The objective of this literature review was to study the work undertaken by previous investigators which pertained to the denitrification of low strength wastewaters. Several processes have been discussed with emphasis upon the submerged or packed bed filter.

The literature presented has been divided into the following areas: 1) fundamental concepts of nitrogen removal; 2) biological denitrification processes; and 3) the submerged filter process for denitrification.

A. FUNDAMENTAL CONCEPTS OF NITROGEN REMOVAL

Nitrogen removal can be accomplished by several methods. These methods are shown in Table I. Ammonia removal alone will solve several of the aforementioned problems such as the increased oxygen demand on streams, fish kills due to ammonia discharge, and the reduced effectiveness of chlorination.

Table I. Nitrogen Removal Processes

Biological	Chemical	Physical
Aerobic nitrification	Ion Exchange	Ammonia Stripping
Anaerobic denitrification	Electrochemical	Reverse Osmosis
Algal harvesting	Electrodialysis	Distillation
	Breakpoint Chlorination	Land Application

Recent technology has produced several processes designed to remove ammonia or to convert ammonia nitrogen to nitrate nitrogen through biological, chemical or physical mechanisms. These processes include biological nitrification, algal harvesting, ion exchange, ammonia stripping, breakpoint chlorination and distillation. In order to utilize a denitrification system effectively the influent to the system must be well nitrified, that is, the ammonia nitrogen must have been converted to nitrate nitrogen. Several of these processes of ammonia conversion will be discussed.

1. Biological Nitrification

Biological nitrification is a process in which ammonia nitrogen is oxidized by autotrophic nitrifying bacteria such as Nitrosomonas and Nitrobacter to nitrate nitrogen. The following equations give the chemical reactions which occur in a biological nitrification process due to the microorganisms and cellular synthesis. (11)

$$\text{Step 1} \quad NH_4^+ + 3/2\ O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2H^+ + H_2O \qquad \{1\}$$

$$\text{Step 2} \quad NO_2^- + 1/2\ O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- + 2H^+ + H_2O \qquad \{2\}$$

$$\text{Synthesis} \quad 4CO_2 + HCO_3^- + NH_4^+ + H_2O \longrightarrow C_5H_7NO_2 + 5O_2 \qquad \{3\}$$

The overall reaction used to describe the autotrophic conversion of the ammonium ion (NH_4^+) to nitrate is as follows:

$$\text{Overall} \quad 22NH_4 + 37\ O_2 + 4CO_2 + HCO_3 \longrightarrow C_3H_7NO_2 + 21\ NO_3^- + 20\ H_2O + 42H^+ \qquad \{4\}$$

The techniques available for conducting biological denitrification are essentially the same as those used for carbonaceous BOD removal, activated sludge (suspended growth), the trickling filter and the rotating disk.

The biochemistry of the activated sludge nitrification process imposes several requirements on the system. The microorganisms carrying out the reactions require up to 8 lbs (3.6 kg) of alkalinity and 4-5 lbs (1.8-2.3 kg) of available oxygen for each pound of ammonia nitrogen oxidized. The pH of the waste should be in the optimum range of 7.8 to 8.9. A low level of BOD (40-50 mg/l) is also a desirable feature of the waste stream. The microorganisms are sensitive to such toxic materials as cyanides, phenols, mercaptans, and heavy metals. (12)

Other critical operating parameters of biological nitrification include temperature (optimum 20-25°C, the reaction stops below 5°C), and solids retention time (SRT, 5-10 days). If the SRT of the system drops below a critical minimum SRT, based on temperature, the nitrifying organisms will wash out of the system. The mixed liquor volatile suspended solids (MLVSS) of the system should range between 1500 and 2500 mg/l. The dissolved oxygen concentration has also been found to be critical. In general, a minimum D.O. range of 2-4 mg/l must be present in the aeration tanks for efficient nitrification to occur. (12)

A fixed growth system such as the trickling filter offers certain advantages such as ease of operation, greater stability, and eliminates dependence on the settling properties of the mixed liquor. Trickling filters can be constructed with plastic media. (13), (14), (15) Plastic trickling filter media are used primarily to take advantage of the large uniform surface area per unit volume ratios available, to provide a high void ratio for adequate oxygen transfer and to alleviate the plugging problems sometimes associated with trickling filters. Recycle of final effluent is commonly used to maintain hydraulic loadings in the range of 0.5 to 5 gpm per square foot (0.34-3.4 lps/m^2). Recycle of the final effluent is a means of achieving consistent stabilized operation rather than high level performance.

Rotating disk systems consist of tanks with large, up to 12 ft (3.66 m) diameter, discs mounted on shafts. Shafts may be up to 25 ft (7.6 m) long with polystyrene or polyethylene discs packed along their entire length. Biological growth occurs on the discs' surface. No recycling is normally used with these devices. The discs commonly rotate at a peripheral speed of about 60 ft per min (18.29 m per min).

A major difference between fixed growth and suspended growth systems is that no solids recycle is necessary for the fixed growth system. Settling characteristics and

capture of mixed liquor solids are, therefore, less critical to the operation of a fixed growth nitrification system. For trickling filters, however, final effluent may be recycled during periods of low flow to maintain a minimum hydraulic loading on the system. (15)

While SRT determines whether nitrifying organisms can survive or not in a suspended growth system, it is not directly controllable, nor as important in a fixed growth system. In a fixed growth system, microbial population dynamics tend to be the factor which determines whether or not the nitrifying organisms survive; if the environment favors these growths, they will grow. In a suspended growth system, this means having enough oxygen and retaining the microbial mass (sludge) in the system long enough to prevent the organisms from being washed out. In a fixed growth system it generally means that the BOD must be low enough so that the nitrifying bacteria can successfully compete with the heterotrophic (BOD consuming) microorganisms for a limited amount of media surface. Typically, this means that nitrifying bacteria do not start to proliferate until the average carbonaceous BOD of the wastewater stream coming in contact with a given area of media is less than 20 to 30 mg/l. This may occur in a physically separate stage, as in the case of a multistage rotating disk system or multistage trickling filter process. It may also occur uniformly

within one completely mixed stage, as in the case of a single stage rotating disk or a single stage trickling filter with high recycle rates, or at the end of a plug flow single stage system, as in the bottom part of a single stage trickling filter. Thus, as opposed to the two stage suspended growth system which requires a minimum BOD to maintain a SRT, fixed growth systems require that the maximum BOD in the nitrifying section not exceed 20 to 30 mg/l. High BOD values may severely inhibit or prevent nitrification through competition for nutrients between the nitrifying organisms and heterotrophic organisms. (16)

The other parameters of importance are the same as those important to the suspended growth system; namely, pH, temperature, dissolved oxygen, and toxic materials. Thus, precautions relating to these parameters are similar.

2. Algal Harvesting

Algal harvesting utilizes the same principal as in biological nitrogen removal through assimilation by the transformation of soluble and colloidal nitrogen to algal cell tissues. The following equation represents the growth of cell tissue in such a system. (11)

$$106\ CO_2 + 81\ H_2O + 16\ NO_3 + HPO_4 + 18H + \text{Light} \longrightarrow C_{106}H_{181}O_{45}N_{16}P + 150\ O_2 \quad \{5\}$$

This process is theoretically feasible where large quantities of nitrate are to be removed. Carbon dioxide may have to

be added as a supplementary carbon source in some wastewaters. The major disadvantages to this process are the large land requirements and the costs associated with harvesting and disposal of the algae. (11)

3. Ion Exchange

Ion exchange for removal of ammonia nitrogen is a less common process than biological nitrification, but it is currently being installed in several municipal wastewater treatment plants. (17) In this process, ammonia in the wastewater is replaced by sodium or calcium previously combined with the exchange resin.

Ion exchangers are similar in appearance to conventional water treatment plant gravity or pressure filters. Their operation requires taking them off line periodically for regeneration of the ion exchange media. The natural zeolite, clinoptilolite, is currently being used as the exchange media in the process because of its selectivity for ammonium ion over calcium, magnesium or sodium ions. Ion exchangers are not ordinarily designed to accept suspended solids, so adequate filtration preceding them is necessary. (16)

The regeneration of clinoptilolite is currently accomplished by contact with a sodium chloride-caustic (or lime) brine. Since the ammonia is concentrated in the regenerant brine, it requires subsequent disposal. One such disposal process involves electrolysis of the brine. Another method

of brine disposal currently being considered is air stripping of ammonia and recirculation of the regenerant solution with lime and sodium chloride makeup. (17)

4. Breakpoint Chlorination

Breakpoint chlorination is another means of removing ammonia. In this process ammonia is converted primarily to nitrogen gas. High chloride concentrations are a side effect (1 mg/l of chloride per mg/l of chlorine added). Since approximately 8 to 10 mg/l of chlorine are required per mg/l of ammonia nitrogen removed, 160 to 200 mg/l of chlorine would be required for a water containing 20 mg/l of ammonia nitrogen. (16)

Proper mixing and pH control are critical for breakpoint chlorination. At approximately pH 6 or below, odiferous NCl_3 will be formed. At approximately pH 8 or above, nitrate will be formed. Insufficient mixing would allow pockets of high or low pH to exist with the aforementioned effects.

During breakpoint chlorination, at least 14.3 mg/l of alkalinity are lost per mg/l of ammonia nitrogen oxidized, if liquid chlorine is used. If hypochlorite is used, only about 3.6 mg/l of alkalinity will be lost per mg/l of ammonia nitrogen oxidized. If breakpoint chlorination follows nitrification, enough alkalinity must be added to maintain the pH close to 7.0 prior to chlorine addition.

5. Biological Denitrification

Denitrification is a microbial process in which nitrogen in wastewater is converted from an objectional form to

a non-objectional form; that is, nitrogen in the nitrate and nitrite forms is reduced to molecular nitrogen. This molecular nitrogen then may leave the system as a gas. (8), (18), (19)

Figure 2 is a diagram of the main biological processes involving nitrogen. The left portion of the diagram shows the reduction of nitrate through nitrite to elemental nitrogen. This is the denitrification process.

The reactions in Figure 2 are defined as follows: (20)

Nitrification - the oxidation of ammonia to nitrate, via nitrite, is carried out by a limited number of autotrophic bacteria genera.

Assimilation - the conversion of nitrate to cellular, organic nitrogen via ammonia.

Dissimilation - the oxidation of carbon compounds at the expense of nitrate, which acts as the alternative hydrogen acceptor to oxygen.

Denitrification - a special case of dissimilation in which gaseous N_2 and/or N_2O are the end products.

Deamination and lysis - in dying cells, lysis of the cell wall occurs and ammonia is formed from organic nitrogen compounds by various deamination reactions.

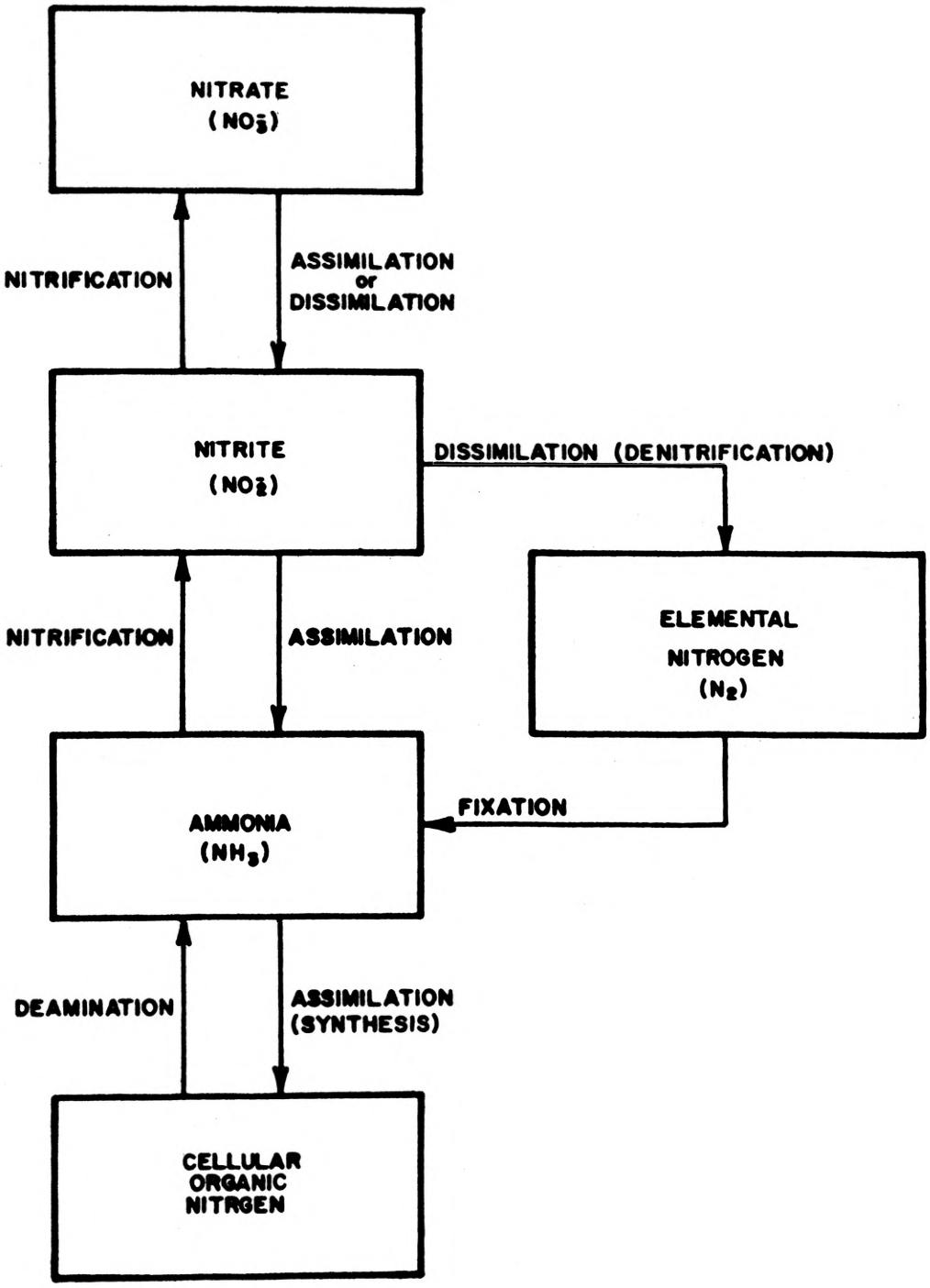


FIGURE 2. THE PRINCIPAL BIOLOGICAL PROCESSES INVOLVING NITROGEN.

There are numerous types of bacteria capable of performing the denitrifying process. Some of these are the following common facultative bacteria; genera Pseudomonas, Denitrobacillus, Achromobacter, Micrococcus, Spirillum, and Bacillus. (9), (18), (19), (20) In the absence of molecular oxygen, these organisms use nitrate as a terminal electron acceptor while oxidizing organic matter for energy. (21)

Denitrification includes the dissimilatory nitrate reduction process and results in removal of the nitrogen as gaseous end products, primarily molecular nitrogen. In the dissimilatory nitrate reduction process, nitrate serves as the terminal exogeneous hydrogen acceptor for the oxidation of an organic substrate. Nitrate reduction is closely related to the use of oxygen as a hydrogen acceptor. The electron transport system is the same in both cases except for the terminal enzymes. In nitrate reduction, the enzyme nitrate reductase replaces cytochrome oxidase. (20), (22)

When dissolved oxygen is present in the system, a noncompetitive inhibition of nitrate reduction occurs. That is, the rate of electron transport to oxygen is much greater than to nitrate. As a result, when oxygen is available, no apparent dissimilatory nitrate reduction takes place until the system becomes effectively anaerobic. (20), (22)

The denitrifying ability of the various microorganisms differs. Some bacteria reduce nitrate to nitrite only, some reduce nitrites to molecular nitrogen only, and some reduce both nitrate and nitrite to molecular nitrogen. (18)

With a naturally occurring heterogeneous population, all these modes of denitrification will probably occur. Therefore nitrites may or may not occur as an intermediate. Several investigators report no significant buildup of nitrite. (8), (19), (22)

When methanol is used as the organic carbon source the following equations describe the two-step process of denitrification and the summary reaction. (8), (9), (18), (19), (23)

First step: $NO_3^- + 1/3\ CH_3OH \rightarrow NO_2^- + 1/3\ CO_2 + 2/3\ H_2O$ {6}

Second step: $NO_2^- + 1/2\ CH_3OH \rightarrow 1/2\ N_2 + 1/2\ CO_2 + 1/2\ H_2O + OH^-$ {7}

Summary Reaction: $NO_3^- + 5/6\ CH_3OH \rightarrow 1/2\ N_2 + 5/6\ CO_2 + 7/6\ H_2O + OH^-$ {8}

Equations 6 through 8 indicate the quantity of organic material required for the denitrification reaction only. Additional substrate must be present to satisfy bacterial growth, energy, and cell maintenance requirements. It can be seen from these equations that the presence of the organic carbon source is critical in the denitrification process. Assuming a two-step process, as previously described, if only 40 percent of the total carbon requirement were added, the result might be the conversion of nitrate to nitrite, with no effective nitrogen removal.

McCarty, et al. investigated the use of various carbon sources in the denitrification process. The carbon sources used were methanol, sugar ($C_{12}H_{22}O_{11}$), acetone, ethanol and acetic acid. (18)

Methanol was selected as the best source of carbon for the following reasons: acetic acid and ethanol are currently more expensive on an equivalent basis than either acetone or methanol. However, the higher vapor pressure of acetone in water made methanol the most advantageous choice.

McCarty, et al. (18) also evaluated carbon sources using a consumptive ratio (ratio of the total quantity of an organic chemical consumed during denitrification to the stoichiometric requirement). The higher the ratio is, the greater chemical requirements for biological synthesis.

The consumptive ratio combined with half reactions for nitrate, nitrite and methanol gives the following balanced equations for the overall denitrification process:

Overall nitrate removal;

$$NO_3^- + 1.08\ CH_3OH + H^+ \longrightarrow 0.065\ C_5H_7O_2N + 0.47N_2 + 0.76\ CO_2 + 2.44\ H_2O \quad \{9\}$$

Overall nitrite removal;

$$NO_2^- + H^+ + 0.67\ CH_3OH \rightarrow 0.04\ C_5H_7O_2N + 0.47\ CO_2 + 0.48\ N_2 + 1.7\ H_2O \quad \{10\}$$

Overall deoxygenation;

$$O_2 + 0.93\ CH_3OH + 0.056\ NO_3^- + 0.056\ H^+ \longrightarrow 0.56\ C_5H_7O_2N + 0.65\ CO_2 + 1.69\ H_2O \quad \{11\}$$

From equations 9, 10, and 11 the quantity of methanol required for denitrification can be evaluated. On a weight basis this can be expressed by the following equation.

Methanol requirement:

$$Cm = 2.47\ No + 1.53\ N_1 + 0.87\ DO$$

where Cm = required methanol concentration, mg/l

N_o = initial nitrate nitrogen concentration, mg/l

N_1 = initial nitrite nitrogen concentration, mg/l

DO = initial dissolved oxygen concentration, mg/l

Seidel and Crites (9) reported that a methanol to nitrate nitrogen ratio of 1.9:1 is required to convert nitrate nitrogen to nitrogen gas. However, an additional 25 percent methanol must be added to allow for biological synthesis. It has also been reported that using a complete mix denitrification process 0.67 lb of methanol are required to remove 1 lb of influent dissolved oxygen. (23)

The biological synthesis can also be expressed on a weight basis by the following equation. (18)

Biomass production

$$C_b = 0.53\ N_o + 0.32\ N_1 + 0.19\ DO$$

where C_b = biomass production, mg/l.

Biomass production can be used to roughly evaluate yield data for the submerged filter. Yield has been defined as mg suspended solids produced/mg substrate removed. Moore and Schroeder (22) reported yield values of 0.6 mg/mg nitrate nitrogen removed, while Stensel, et al. (8) reported 0.18 mg/mg COD removed. These results agree with yield values reported by McCarty, et al. (18) Yield characteristics are important for comparison of the denitrification process with the activated sludge process, comparison and selection

of alternative carbon sources for denitrification, and for evaluation of different process flow diagrams for denitrification. (24) Painter (20) reported that anaerobic systems have the lowest yields, while nitrate reduction systems have yields lower than aerobic but higher than anaerobic systems.

The low solids yield, exemplified by anaerobic and nitrate reduction systems, is a desirable characteristic of these processes in that a system with low solids yield minimizes the quantity of sludge produced. This is an especially important factor in the field today when such a large portion of the total cost of building and operating a plant is involved with solids handling, dewatering and disposal.

The importance of yield in considering alternate carbon sources for denitrification was demonstrated by McCarty, et al. (18) in his work with consumptive ratios. Higher ratios mean higher yields or greater chemical requirements for synthesis. (24)

B. DENITRIFICATION PROCESSES

Denitrification can be accomplished by several methods. In applying a particular process to any situation, certain factors must be taken into consideration. These include degree of treatment required, type of ultimate disposal problems which may result, operational problems, environmental compatibility of the process, and economic feasibility.

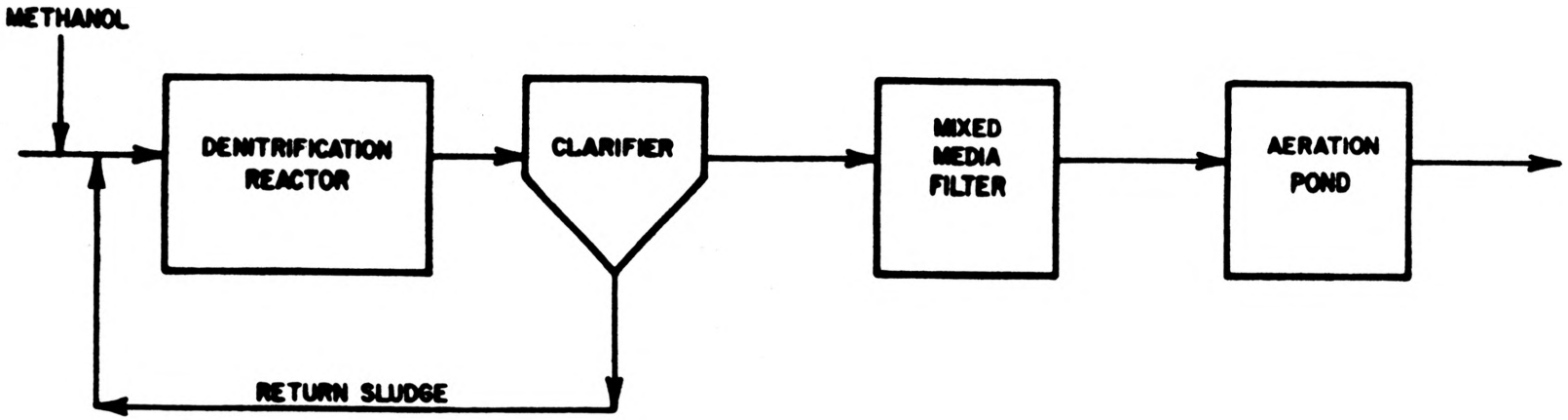
The methods as shown previously in Table I included biological, chemical, and physical processes. Several of the biological processes will be discussed below. These processes include the submerged filter, complete mix reactors, and lagoons with recycle, all of which come under the heading of anaerobic denitrification (4), (12), (25), (26)

1. Completely Mixed Process for Denitrification

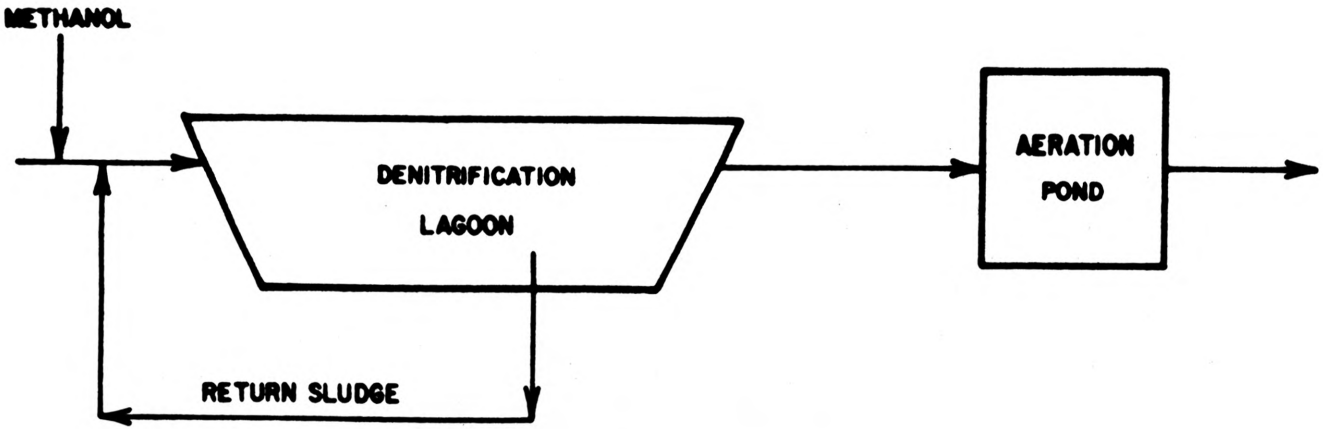
There have been several investigations of the completely mixed process of denitrification. (8), (22), (23) The recycle of solids in a pilot plant system as reported by Mulbarger (23) is illustrated in Figure 3a. Other systems effectively removed nitrates from the waste stream without solids recycle in laboratory investigations.

Stensel, et al. (8) proposed kinetic equations for the denitrification process. A continuous feed, suspended growth reactor without recycle was used in the study. Kinetic-based design criteria were determined which would yield minimal effluent COD concentration as well as minimal nitrate nitrogen concentration. The design criteria were: 1) solids retention time (SRT), 2) solids production rate, and 3) methanol requirements. Temperature was also investigated.

The following steady-state equations were used to describe the complete-mix continuous flow, no solids recycle system used in the study. (8)



A) COMPLETE MIX SYSTEM WITH RECYCLE (23).



B) LAGOON WITH RECYCLE (2)

FIGURE 3. SCHEMATIC DIAGRAMS OF SUSPENDED GROWTH DENITRIFICATION PROCESSES.

Effluent substrate concentration

$$S = \frac{K_s \{1 + b(SRT)\}}{SRT\ (YK - b) - 1} \quad \{14\}$$

Reactor specific substrate utilization rate

$$U = \frac{KS}{K_s + S} \quad \{15\}$$

Effluent microbial solids concentration

$$X = \frac{Y(S_o - S)}{1 + b(SRT)} \quad \{16\}$$

Solids retention time

$$SRT = \frac{VX}{QX} = HRT \quad \{17\}$$

$$SRT^{-1} = YU-b \quad \{18\}$$

where:

SRT = microbial solids retention time, days

HRT = hydraulic retention time, days

S = effluent substrate concentration, mg/l

X = effluent microbial solids concentration, mg/l

U = specific substrate utilization rate, day^{-1}

K = maximum specific substrate utilization rate, day^{-1}

K_s = Michaelis-Menten constant, substrate concentration where U = 1/2K, mg/l

Y = yield coefficient, mg suspended solids produced per mg substrate removed

b = microbial solids decay coefficient, day^{-1}

Q = liquid flow rate through reactor, l/day

V = reactor volume, l

S_o = influent substrate concentration, mg/l

A series of growth rate limiting substrate determinations were made to establish whether methanol or nitrate nitrogen was the limiting substrate. The results indicated that the organic matter, or methanol, was the limiting substrate as described by the kinetic model. Nitrate nitrogen was not the growth rate limiting substrate when excess methanol was present unless the nitrate nitrogen concentration approached 1 mg/l. That is, as long as sufficient methanol is added to the process, nitrate will be reduced to limits approaching 1 mg/l. (8)

In the study of temperature effects, it was shown that at a SRT of 4 days there was no appreciable difference between systems run at 20°C and 30°C, but at 10°C a SRT of 8 days would be needed to achieve similar minimal COD in the effluent.

In evaluating yield and methanol requirements, Stensel, et al. (8) basically agreed with values reported by McCarty, et al. (18) He concluded that nitrate nitrogen removal efficiency can be determined by controling the SRT and the quantity of organic carbon added to the process. Stensel proposed the following equation for nitrate removal efficiency.

$$N_1 = \left[\frac{K_s \{1 + b(SRT)\}}{SRT(YK - b) - 1} - 1.5\ D.O.\right] 3.46\ N_o(100) \quad \{19\}$$

where N_1 = NO_3-N removal efficiency, per cent

D.O. = dissolved oxygen, mg/l

N_o = influent NO_3-N concentration, mg/l

Other symbols used as previously defined.

Moore and Schroeder (22) used the same type of system as Stensel and reported that a SRT of 6 days was the optimum for denitrification, but at a SRT of 9 days the total methanol requirements were lower.

2. Denitrification Lagoons with Recycle

McCarty, (2) in a pilot plant study of agricultural drainage water ponds 6 and 11 feet deep with recycle of effluent solids, reported 90 percent removals of nitrate nitrogen with a 10 day SRT and 80 percent removals of nitrate nitrogen with a 5 day SRT. During winter months, lower efficiencies were reported, which possibly reflected the influence of lower temperatures. He proposed increasing detention times to increase nitrate nitrogen removal efficiencies during the winter periods. In uncovered ponds, he reported 50-60 percent nitrogen removals. The probable causes of these low efficiencies were surface reaeration, wind-mixing and possibly thermally produced water turn-over. Figure 3b illustrates a flow diagram of the proposed lagoon system.

C. THE SUBMERGED FILTER PROCESS FOR DENITRIFICATION

As previously stated, conventional anaerobic processes are not recommended for treating wastes of less than 1 percent biodegradable organic material. Anaerobic activated sludge, or complete mix systems as described in the previous section, can treat low strength wastes efficiently, but settling and recycling of effluent solids are necessary to

maintain the high biological mass needed for efficient treatment. For soluble wastes, a significant fraction of the microbial mass may remain dispersed, the biological solids are hard to settle and recycle, and high treatment efficiencies are difficult to maintain.

An important operating parameter of any biological waste treatment process is the SRT. In order for a sufficient microbial mass to develop, which will effectively treat low strength waste, sufficiently long SRT's are necessary. When considering a completely mixed or anaerobic contact process, maintenance of a long SRT usually requires efficient solids separation and recycle.

The submerged filter has the following definite advantages over these other systems (6):

1. It is ideally suited to treatment of soluble wastes as it will provide high SRT and requires no pretreatment such as clarification.
2. No effluent or solids recycle is necessary. The biological solids remain in the filter for extended periods and are only discharged intermittently with the effluent.
3. The accumulation of high concentrations of active solids in the filter permits the treatment of dilute wastes at nominal temperatures. Heating is not required as in most other anaerobic processes to maintain high treatment efficiencies.

4. Very low volumes of sludge are produced. The effluent is essentially free of suspended solids (SS) and sludge wasting is almost non-existent.
5. The submerged filter seems to utilize methanol more efficiently than a complete-mix system. The difference is attributed to differences in process yield. (27)
6. Reduced biological nutrient requirements are exhibited. (7)
7. Upward flow through the filter forces gas bubbles out with the effluent and prevents gas binding. (9)

Tamblyn and Sword (3) investigated the feasibility of the anaerobic filter for denitrification under field conditions. Included in their studies were investigations of medium size, texture, and sorptive quality, long term operation, hydraulic retention time and comparison of predicted and actual quantities of organic carbon required.

It was noted that medium surface texture and sorptive quality did not appreciably affect removal efficiencies. Also, there were no apparent differences in removal efficiencies for media of the same type but of differing size.

When sand was used as the media, it was found that the microbial mass in the filter accumulated to a point where a surge of water had to be forced through the filter to break the clog, with a resultant temporary drop in efficiency from 90 to 34 percent. With 1 in. (2.54 cm) aggregate this problem did not arise. Short circuiting problems with flows

through the sand filters also were noted. Using media with diameters of 3/8 and 5/8 in. (0.95 and 1.59 cm) no short circuiting or plugging was experienced, but high influent pressures had to be maintained, making those sizes of media less economical to use than the 1 in. (2.54 cm) media.

Temperature effects were noted by the fact that at lower temperatures a greater percentage of the filter was utilized to achieve the same degree of treatment than at a higher temperature.

Tamblyn and Sword concluded that the anaerobic filter was feasible under field conditions for long term operation without backwashing. The use of media of less than 1 in. (2.54 cm) resulted in high head loss and low nitrogen removal. Efficient removals could be obtained at hydraulic retention times (HRT's) of 0.5 to 2.0 hr depending on the temperature, with the longer HRT required for lower temperature. Finally, McCarty's equation (Eq 12) for methanol requirements for denitrification was verified as being applicable to anaerobic filters in the field.

In a study of the submerged filter using plexiglass Rashig rings as media, Requa and Schroeder (19) determined kinetic equations for denitrification very similar to those proposed by Moore and Schroeder (22) in their study of a complete-mix system.

The kinetic equations proposed by Requa and Schroeder are the following:

$$R_{NO_3^-} = \frac{-u\ C_{NO_3^-} - X}{K + C_{NO_3^-}} \quad \{20\}$$

$$C_{NO_3^-} = (C_{NO_3^-})_i + \tau\ R_{NO_3^-} \quad \{21\}$$

$$W(C_{NO_3^-})_{N-1} + V\ R_{NO_3^-} = W(C_{NO_3^-})_N \quad \{22\}$$

$$u = \frac{(C_{NO_3^-})_{N-1} - (C_{NO_3^-})_N}{\tau\ X_N} \quad \{23\}$$

where R_{NO_3} = rate of nitrate-nitrogen removal, mass nitrogen/time/volume

C_{NO_3} = concentration of nitrate nitrogen in the reactor increment, mass/volume

X = mixed liquor suspended solids (MLSS) concentration, mass/volume

u = rate coefficient corresponding to maximum specific removal rate, $time^{-1}$

K = saturation coefficient, mass/volume

τ = incremental HRT, time

W = volumetric flow rate, volume/time

V = incremental reactor volume

N = number of reactors

These equations were based on the assumption that the hydraulics of a submerged filter could be approximated by a series of ideal stirred tanks. Tracer studies showed this assumption was acceptable.

Nitrate removal rate depends on nitrate concentration and the concentration of denitrifying microorganism cells. Thus, any effluent nitrate concentration is theoretically possible at any hydraulic detention time. The choice between utilizing nitrate or cell concentration is usually handled by maximizing cell concentration. An upflow submerged filter is ideal because of the high cell concentrations possible. The major limitation is the hydraulic characteristics of the reactor which effectively set a maximum cell concentration and thus a maximum reaction rate. (19)

Requa and Schroeder (19) concluded that nitrite buildup in the filter was not significant. Therefore a single step reaction can be assumed. Also, the maximum value of u is found at reactor concentrations greater than 2 mg/l nitrate nitrogen, with a value of 0.074 day^{-1}. The fact that removal rates are independent of nitrogen concentration above 2 mg/l is important because the process can be operated at the maximum specific removal rates at low concentrations of nitrogen.

English, et al. (5) investigated both upflow sand and carbon packed bed columns for denitrification in a 0.3 MGD (0.013 m^3/sec) pilot plant. The 16 ft (4.87 m) high filters were filled with either 0.9 mm sand or activated carbon and fed a concentration of 25 mg/l nitrate nitrogen with methanol addition. Four filters were used in series with either sand or carbon as media. Nitrate nitrogen removals

of up to 90 percent were observed with retention times of 10 min per filter stage, or a total HRT of 40 min. In order to keep the influent pressures low, the filters needed to be backwashed at least once a day. Backwash quantities were about 9 percent of the flow. In full scale plants it is anticipated that backwashing would be necessary three times per day to maintain no more than a 25 psi (122 Kg/m^2) headloss between backwashes.

Jeris, et al. (28) studied a system in which fluidized beds of activated carbon were used as the filter media. The following advantages could be realized from the fluidized bed concept: greater surface area available for growth per unit of reactor volume, very small head loss, no danger of clogging, and easier media removal procedures. Flow rates of 0.4, 0.6 and 1.2 gpm (1.5, 2.3, and 4.5 l/min) were used through 12 ft (3.65 m) high volumns with retention times of 3.5 to 10.5 min. Efficiencies of nitrate nitrogen removal were 80 to 90 percent at a methanol to nitrogen ratio of 2.4:1. Influent nitrate nitrogen concentrations averaged from 35 to 40 mg/l. A disadvantage to the system lies in the fact that continued biological growth causes continued bed expansion so that either sloughing or removal of media is necessary.

An interesting fact brought out by Jeris, et al. (28) concerns the noticeable increase in alkalinity within the denitrification system, 18 to 145 mg/l as $CaCO_3$. This was

accounted for by the fact that one mole of hydroxyl ion is produced per mole of nitrate reduced to gaseous nitrogen. As the waste stream passed upwards through the bed and nitrate was reduced, a corresponding increase in alkalinity was noted. There is also a tendency for the pH to increase through the height of the filter. This occurs because 2 moles of hydrogen ions are utilized in reduction of one mole of nitrate to nitrogen gas.

III. EXPERIMENTAL PROCEDURES

Two laboratory scale submerged filters were used in this study. The program of experimentation was designed to evaluate the performance of the filter when used to treat a high nitrate synthetic waste such as may be found in agricultural subsurface drainage waters.

This chapter describes the design of the laboratory filters and feed system, the synthetic waste, and the analytical procedures employed during the course of the study.

A. LABORATORY FILTERS

Laboratory filters (Figure 4) were designed and constructed by Dennis (29) of Plexiglass* columns, 6 in. (0.1525 m) in outside diameter (OD), 3 ft (0.915 m) high, with an inside diameter (ID) of 5.5 in. (0.14 m). The total volume of the empty cylinder was 0.5 cu ft (14.25 l). The base of the column was designed to disperse the influent uniformly across the filter bottom. This was accomplished by drilling eight 1/4 in. (0.635 m) diameter holes evenly spaced around a 4 in. (0.102 m) diameter circle in a dispersion plate at the lower end of the column. This plate rested immediately above an open space 4 in. (0.102 m) in diameter and 1/8 in. (0.317 cm) deep in the base of the column. See Figure 4. With this configuration the raw waste entered at the center of this open circular space

* A product of Cope Plastics, St. Louis, Mo.

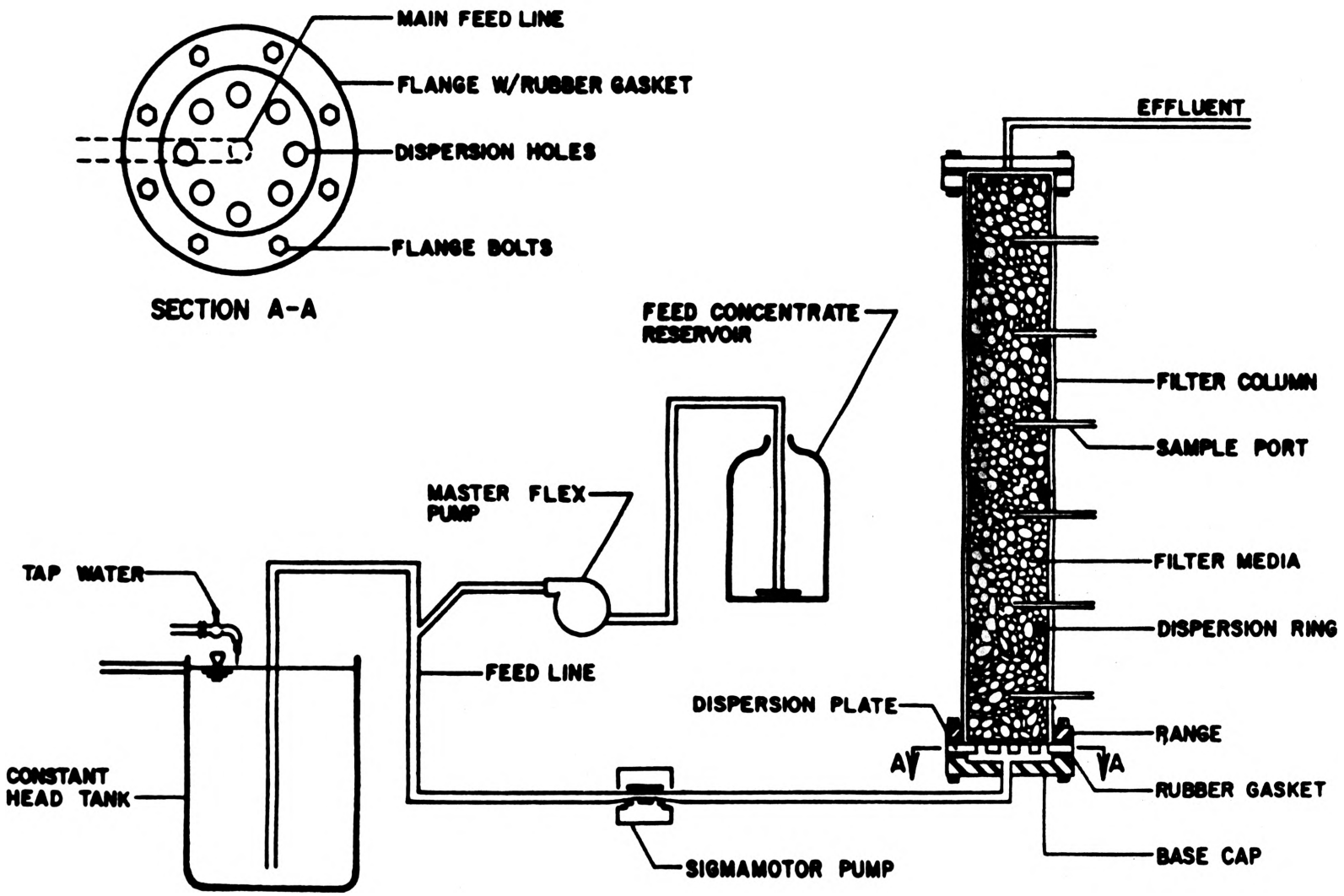


FIGURE 4. SCHEMATIC DIAGRAM OF SUBMERGED FILTER AND FEED SYSTEM, AFTER DENNIS.(29)

and flowed upward through the holes in the dispersion plate.

Sampling ports were placed at 6 in. (0.1525 m) intervals throughout the column height with additional ports 3 in. (0.0765 m) from the top and base of the filter. These sampling ports were connected to tubes which extended to the center of the column. The sampling ports were made of 1/8 in. (0.318 cm) ID Plexiglass tubing and were sealed into the wall of the column with rubber grommets to give a water-tight yet slightly flexible joint. The base and top caps of the filter were bolted to flanges which were cemented firmly and flush to the top and bottom of the column.

Each column was filled with smooth quartzite stone, 1 to 1.5 in. (2.54-3.82 cm) in diameter. Dispersion rings, made of 5/8 in. (1.59 cm) OD vinyl plastic tubing were placed at 1 ft (0.306 m) intervals to prevent short circuiting of the waste flow through the large void spaces formed at the rock-column wall boundary. Each filter then had a porosity of 0.47 and a liquid volume of 0.22 cu ft (6.25 l). (29)

B. FEED SYSTEM

Feed concentrate solutions for the submerged filters were made daily from stock solutions of the various constituents which are presented later and diluted to 6:1 with tap water in 2.5 gal (9.462 l) Pyrex bottles. The feed concentrate was drawn from the bottom of the bottles through

feed lines made of Tygon tubing by a Masterflex* Variable Speed peristaltic pump.

The feed concentrate was pumped through a glass "Y" fitting into a 1/4 in. (0.635 cm) diameter Tygon tube where it was mixed with tap water being pumped from a constant head tank by a low speed Sigmamotor Model T8** peristaltic pump.

A single Masterflex pump was used to pump the feed concentrates, while two Sigmamotor pumps were used to vary the flow rates to the two filters.

The filters were housed in a walk-in environmental chamber***, which was maintained at 35°C. The feed system was set up outside the environmental room at room temperatures about 20°C to retard biological assimilation of the feed concentrates prior to their introduction into the filter units.

C. SYNTHETIC WASTE

The synthetic waste used in this study was made from concentrated solutions of methanol, potassium nitrate, and inorganic nutrients. Typical feed concentrations are shown in Table II after Stensel. (8) Table III shows typical values of hydraulic flow rate and loading rates used in the investigation.

---

*A product of Cole-Parmer Instrument Co., Chicago, Ill.
**A product of Sigmamotor, Inc., Middleport, New York.
***Environ-Room, Cat. No. 751AX, manufactured by Lab-Line, Inc., Melrose Park, Ill.

Table II. Synthetic Feed

Feed Constituent	Quantity (mg/l)
Methanol COD	120
Nitrate Nitrogen	30
$MgSO_4 \cdot 7H_2O$	1
$FeCl_3 \cdot 6H_2O$	1
$MnSO_4 \cdot H_2O$	1
$CaCl_2 \cdot 2H_2O$	1
KH_2PO_4	17.5

D. ANALYTICAL PROCEDURES

During the course of this investigation analyses were performed to determine the chemical and physical characteristics of the synthetic waste, the effluent, and samples withdrawn at sampling ports throughout the height of the filters. The following is a description of the analytical methods used.

1. Sampling

Samples were withdrawn by gravity flow through the sample ports provided in the filter. The order of liquid withdrawal was from top to bottom of the filters. In this manner, an undisturbed sample could be obtained at each level of filter height. Normally a 100 ml volume was collected to obtain a representative sample on which to perform analyses.

Table III. Substrate Loadings Corresponding to Various Combinations of Hydraulic Flow Rates and Waste Strengths

Hydraulic Flow Rate			Substrate Loading Rate (g/cu m/day)**					
HRT*	Liters/ Day	Liters/ Ft^2/Day***	COD (mg/l)			NO_3-N (mg/l)		
			80	100	120	20	30	40
4	37.5	228	210	260	310	50	80	100
2	75	456	420	520	620	100	160	210
1	150	912	840	1040	1240	200	320	420

*Based on 6.25 l liquid reactor volume.

**Based on total reactor volume 14.25 l.

***To convert $l/ft^2/day$ to $l/m^2/day$ multiply by 10.76.

All analyses were performed on fresh samples except in specific instances when samples were stored in a cooler which was maintained at 4°C.

Several times during the course of the study (7, 8, 11, 12, 13 Feb.) samples of the filter influent and effluent were stored in this manner to ascertain whether changes in quality in fact did occur over storage times ranging from 2 to 24 hr.

2. pH

The pH of each sample was measured within 15 min of its withdrawal in order to minimize pH changes caused by loss of dissolved carbon dioxide. A Fisher "Accumet" Model 210 pH meter* equipped with glass electrode was used to make this determination after having been calibrated with a known standard.

3. Alkalinity

Total alkalinity was measured by procedures outlined in Standard Methods. (30, p. 52) Determinations were made on 25 ml samples which were titrated with 0.02 N sulfuric acid to the methyl orange end point.

4. Suspended Solids

Suspended solids content of the filter effluent was determined by gravimetric analysis following procedures outlined in Standard Methods. (30, p. 537) Gooch

*A product of Fisher Scientific Co., Pittsburgh, Pa.

crucibles with grade Whatman CF/A* glass fiber filter pads were used for the determination. Weights of the solids were measured with a Mettler Model H 10 w Analytical Balance**.

5. Chemical Oxygen Demand (COD)

COD was determined by the dichromate reflux method as outlined in Standard Methods. (30, p. 495) A 20 ml sample was used in this analysis. Sulfamic acid was added to the 0.250 N standard potassium dichromate in order to eliminate interference due to nitrite in the sample.

6. Dissolved Oxygen (DO)

DO was determined by the Winkler-azide modification as outlined in Standard Methods (30, p. 477) using 300 ml samples.

7. Nitrogen

Total Kjeldahl nitrogen was determined on filtered and non-filtered samples according to the titration procedure outlined in Standard Methods. (30, p. 244)

8. Nitrate Nitrogen

Nitrate nitrogen was determined in the feed solution, throughout the filter height, and in the effluent by the Brucine nitrate procedure as outlined in Standard Methods. (30, p. 461) The color development was determined at

*A product of W & R Balston, Ltd., England
**A product of Mettler Instrument Corp., Princeton, N.J.

410 mμ on a Spectronic 70* spectrophotometer in 1 cm glass sample cells. Nitrate concentrations were determined by comparing the light absorption of the sample against a calibration curve prepared using standard nitrate solutions. Sample volumes of 10 ml or an aliquot diluted to 10 ml were used.

9. Nitrite Nitrogen

Nitrite nitrogen was determined in the feed solution, throughout the filter height, and in the effluent according to the procedure outlined in Standard Methods. (30, p. 240) The color development was determined at 520 mμ on a Spectronic 70 spectrophotometer in 1 cm glass sample cells. Nitrite concentrations were determined by comparing the light absorption of the sample against a calibration curve prepared using standard nitrite solutions. Sample volumes of 50 ml or an aliquot diluted to 50 ml were used.

E. STARTING THE FILTER

The filter was started according to the method described by Young. (6) A heavy seed, 30g, of sludge from a well operating sewage sludge digester was distributed evenly throughout the lower one-third of the filter. The dose used per unit of volume was equal to twice that used by Young. The unit was operated on a batch basis for the first 30 days as the biological mass in the filter

*A product of Bausch and Lomb Co., Rochester, N.Y.

increased and coated the media throughout the height of the filter. The units were fed once a day with a 3.125 l of feed, or one-half of the liquid volume at high influent pressures so as to push the biological growth higher in the filter. At the end of 30 days the biological growth was noted throughout the filter height and both units were then fed continuously at a 4 hr retention time (HRT).

IV. EXPERIMENTAL RESULTS

In order to achieve the stated objectives of this investigation the laboratory filters were operated at various hydraulic retentions times (HRT), nitrate nitrogen and COD loadings of a synthetic waste. The performance of the filters at the different HRT's and loading rates was determined by monitoring those parameters as discussed in section III.

The results of this experimental study are reported in this chapter in terms of filter efficiency during steady state operation.

A. SYNTHETIC WASTE ANALYSIS

A summary of the physical and chemical characteristics of the synthetic waste as applied to the filters is presented in Table IV. The constituents of the feed solution were similar to those used in an investigation performed by Stensel, et al. (8) Stock solutions of each constituent were made and used to daily replenish reservoirs of concentrated feed solutions. The feed solutions were mixed with tap water which added alkalinity, nitrogen, and dissolved oxygen. An attempt was made to limit the amount of dissolved oxygen in the feed solutions by not allowing the tap water to free fall into the constant head tank.

Table IV. Physical and Chemical Characteristics of the Synthetic Waste

Characteristic	Concentration mg/l
pH	7.3 - 7.8*
Methanol COD	120
Nitrate Nitrogen	30
Nitrite Nitrogen	0 - 0.1
Total Kjeldahl Nitrogen	1 - 4
Alkalinity - as $CaCO_3$	260
Dissolved Oxygen	1.0 - 2.5
$MgSO_4 \cdot 7H_2O$	1
$FeCl_3 \cdot 6H_2O$	1
$MnSO_4 \cdot H_2O$	1
$CaCl_2 \cdot 2H_2O$	1
KH_2PO_4	17.5

*pH units

B. RESPONSE TO STARTING PROCEDURES

In the initial phase of the study, two filters were seeded as described in the previous chapter. The filters were fed a synthetic waste with the major constituents being 30 mg/l nitrate nitrogen and 120 mg/l methanol as COD. Each day an amount of feed solution equal to one-half the liquid volume of the filter was rapidly pumped into the unit. This procedure was used for the initial 30 days of the study until it could be seen that the biological growth in the filter was coating the media and

filling the void spaces.

After this period of microbial growth and attachment to the media both filters were fed continuously at a rate of 37.5 l/day or at an HRT of 4 hours and under the same NO_3-N and COD loading conditions. This was done to provide a control measure to compare the reproducibility of filter performance.

During this period, visual observation of the filters showed rapid accumulation of the microbial solids on the filter media as well as in the voids between the media. There was no noticeable suspended solids in the effluent at this HRT.

In the initial phase of the study, the feed system was evaluated. It was found that the concentration of nitrate nitrogen in the reservoirs deteriorated at 35°C in an environmental chamber. An attempt was made to rectify the situation by maintaining the reservoirs at room temperature, 20°C. Another factor contributing to the deterioration was a layer of the feed constituents which accumulated on the inside of the Tygon feed lines. This was partially remedied by daily compression of the lines to slough off any accumulations and by periodically shutting down the system in order to acid clean and rinse the feed lines. Determination of dissolved oxygen concentrations throughout the system indicated the existence of a predominant facultative environment which seldom became

anaerobic. In some instances low concentrations of dissolved oxygen (less than 0.6 mg/l) were present along with a high quality denitrified effluent.

C. STEADY STATE FILTER PERFORMANCE

Steady state conditions were approximated as shown by consistently high similar nitrate nitrogen removals. At this time it was noted that there was heavy biological growth on the media as well as in the void spaces. Effluent suspended solids began to exit the filters at a rate of approximately 20 mg/l.

1. Response to Loading Changes

COD removal efficiencies ranged from 75 to 97 percent with an average of 87 percent. The COD loading rate did not vary as widely as the nitrate nitrogen loading rate. In only one instance did the COD removal efficiency drop below about 70 percent. Results can be seen in Tables V and VI. Figures 5 through 7 show the response in removal efficiency to variations in influent loadings for both nitrate nitrogen and COD for the three HRT's investigated (1, 2, and 4 hr).

Nitrate nitrogen efficiencies for various nitrogen loading rates (9-735 g/cu m/day) and HRT's (1-4 hr) ranged from 89 to 100 percent with an average of 97 percent. Only once did the removal efficiency drop below 89 percent. These results can be found in Tables VII and VIII. The filters responded favorably at both high and low loading

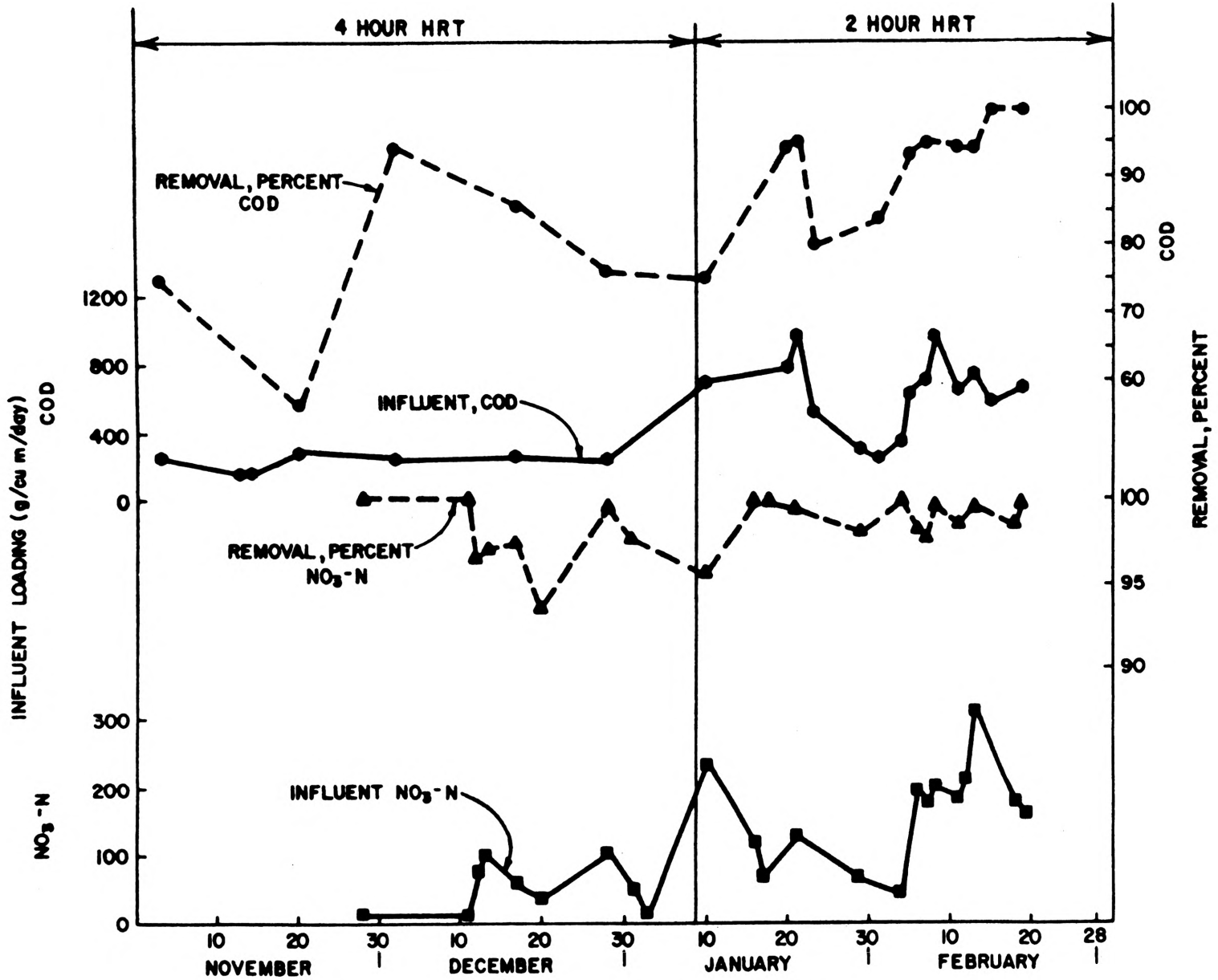


FIGURE 5. FILTER I, INFLUENT NO_3-N AND COD WITH PERCENT REMOVALS

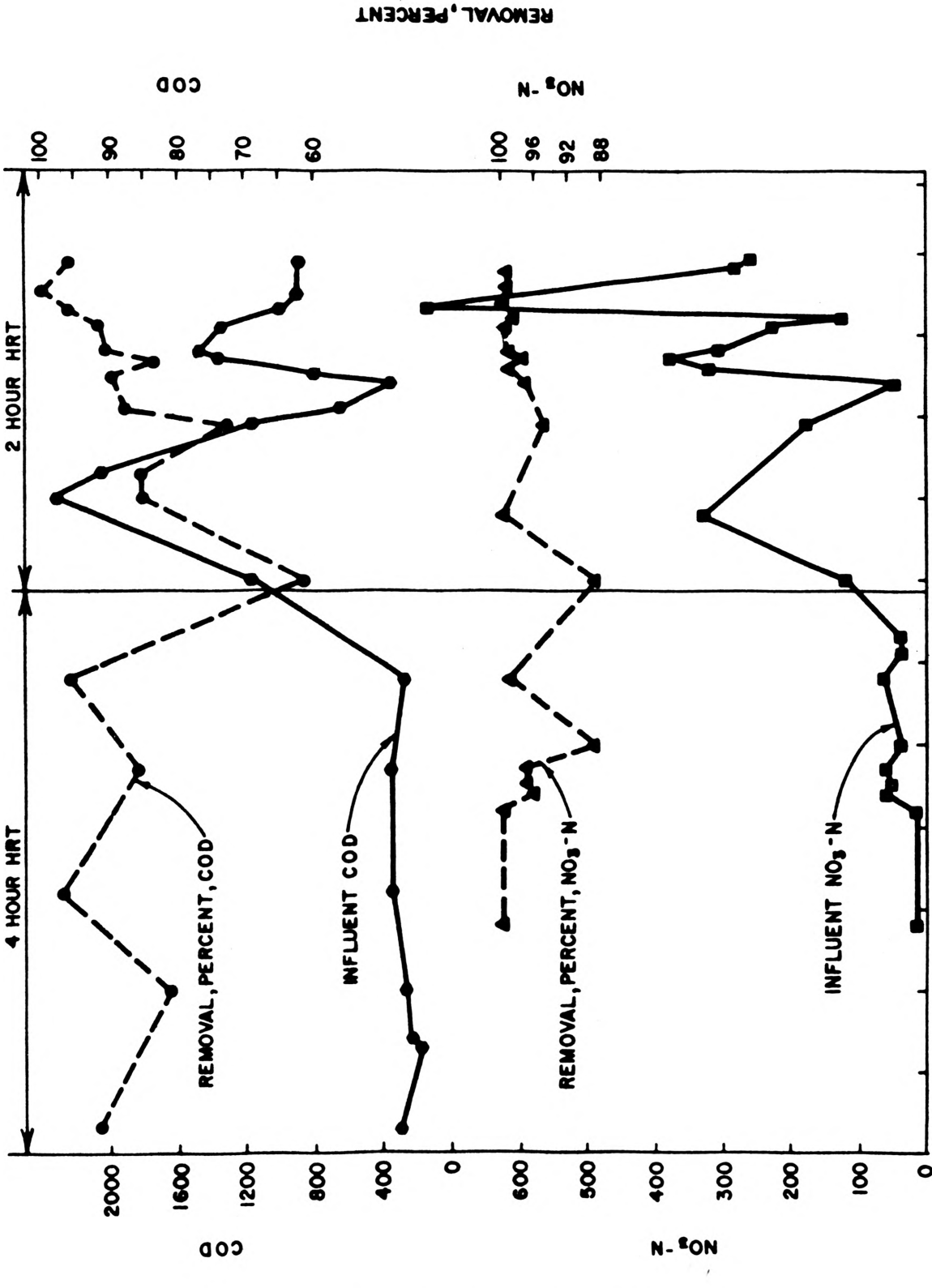


FIGURE 6. FILTER 2. INFLUENT NO_3-N AND COD WITH PERCENT REMOVALS

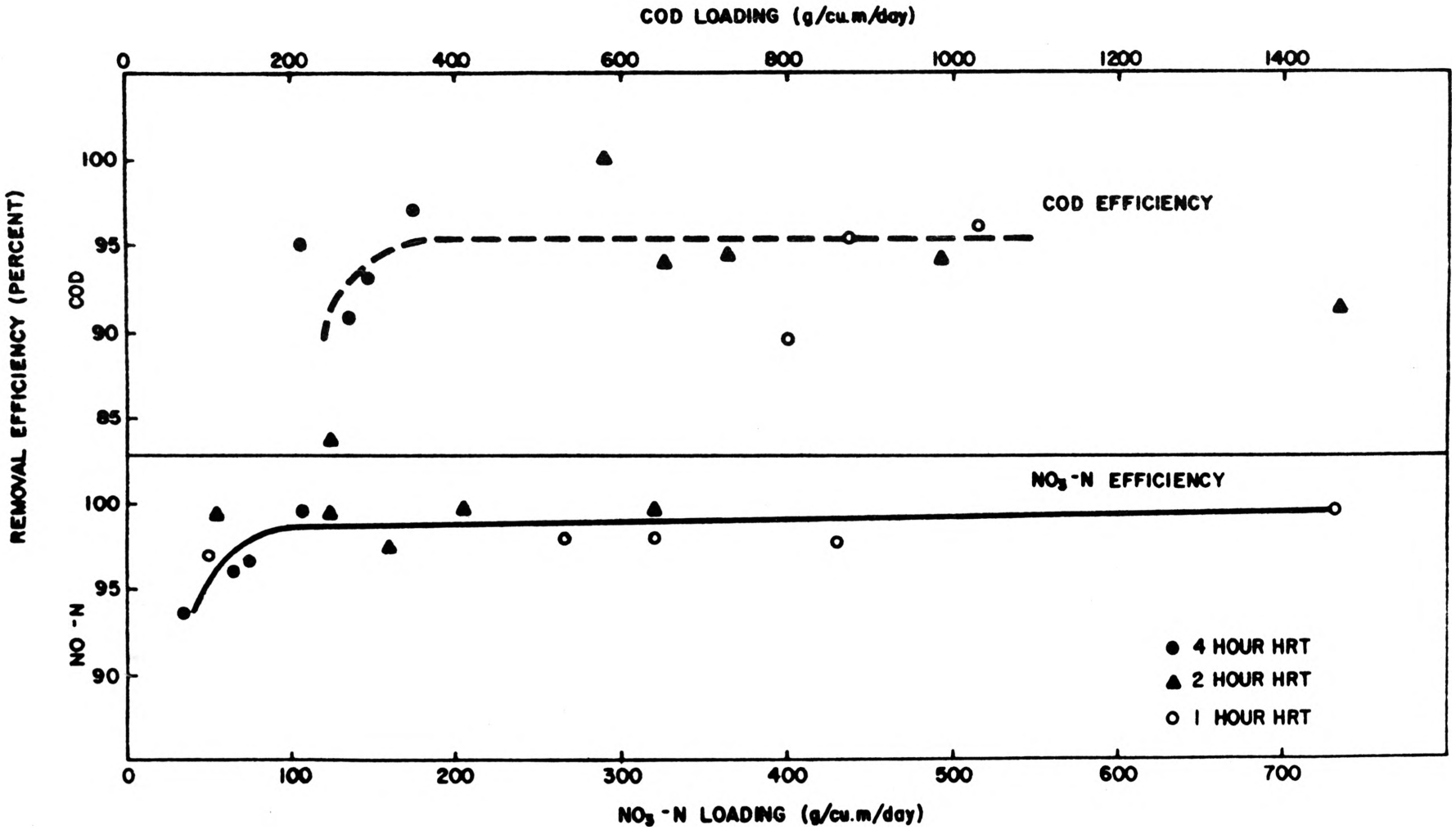


FIGURE 7. REMOVAL EFFICIENCY AND LOADING FOR 4,2,1 HOUR HRT

Table V. Filter 1, COD Removals at 4 and 2 Hour HRT's

Date	Days of Operation*	HRT (hr)	COD Loading Rate (g/cu m/day)	Influent Conc. (mg/1)	Effluent Conc. (mg/1)	COD Removed (%)
3 Nov	2	4	226	85	22.0	74.0
13 Nov	12	4	178	67	-	-
14 Nov	13	4	181	68	-	-
20 Nov	19	4	290	109	51.0	53.0
2 Dec	32	4	272	102	7.6	93.0
17 Dec	47	4	280	105	18.5	82.0
28 Dec	58	4	213	80	3.8	95.0
Avg HRT=4	-	4	234	88	20.6	79.4
10 Jan	2	2	757	142	35.4	75.1
20 Jan	12	2	794	149	7.9	94.7
21 Jan	13	2	957	185	11.1	94.0
23 Jan	15	2	517	97	19.5	80.0
29 Jan	21	2	309	58	62.0	-
1 Feb	24	2	245	46	7.6	83.5
4 Feb	27	2	341	64	-	-
5 Feb	28	2	613	115	8.0	93.0
7 Feb	30	2	677	127	4.0	96.8
7 Feb	30	2	719	135	12.0	91.1
8 Feb	31	2	970	182	15.8	91.3
11 Feb	34	2	650	122	7.6	93.8
13 Feb	36	2	725	136	7.7	94.3
15 Feb	38	2	581	109	0.0	100.0
19 Feb	42	2	687	129	0.0	100.0
Avg HRT=2	-	2	638	120	14.2	91.3

*As established by continuous flow monitoring at specific HRT.

Table VI. Filter 2, COD Removals at 4 and 1 Hour HRT's

Date	Days of Operation*	HRT (hr)	COD Loading Rate (g/cu m/day)	Influent Conc. (mg/l)	Effluent Conc. (mg/l)	COD Removed (%)
3 Nov	2	4	296	111	7.3	93.0
13 Nov	12	4	178	67	-	-
14 Nov	13	4	210	79	-	-
20 Nov	19	4	261	98	18.0	82.0
2 Dec	32	4	352	132	3.8	97.0
17 Dec	47	4	346	130	18.5	86.0
28 Dec	58	4	264	99	3.8	96.0
Avg HRT=4	-	4	272	102	10.3	90.8
10 Jan	2	1	1172	110	42.4	58.6
20 Jan	12	1	2301	216	31.4	85.5
21 Jan	13	1	-	-	-	-
23 Jan	15	1	2025	190	28.0	85.3
29 Jan	21	1	1151	108	31.0	72.0
1 Feb	24	1	650	61	7.6	87.5
4 Feb	27	1	340	32	-	-
5 Feb	28	1	799	75	8.0	89.3
7 Feb	30	1	1332	125	23.8	81.0
7 Feb	30	1	1396	131	19.8	84.9
8 Feb	31	1	1470	138	12.0	91.3
11 Feb	34	1	1343	126	11.5	90.0
13 Feb	36	1	1023	96	3.9	95.9
15 Feb	38	1	899	84	0.0	100.0
19 Feb	42	1	874	82	3.9	95.2
Avg HRT=1	-	1	1169	110	17.2	86.0

*As established by continuous flow monitoring at specific HRT.

Table VII. Filter 1, Nitrate Nitrogen Removals at 4 and 2 Hour HRT's

Date	Days of Operation*	HRT (hr)	NO_3-N Loading Rate (g/cu m/day)	Influent Conc. (mg/l)	Effluent Conc. (mg/l)	NO_3-N Removed (%)
28 Nov	27	4	13	5.0	0.0	100.0
11 Dec	41	4	9	3.5	0.0	100.0
12 Dec	42	4	75	28.0	1.0	96.5
13 Dec	43	4	98	38.0	1.1	97.0
17 Dec	47	4	59	22.0	0.6	97.3
20 Dec	50	4	37	14.0	0.9	93.5
28 Dec	58	4	107	40.0	0.2	99.5
31 Dec	61	4	48	18.0	0.2	97.8
3 Jan	64	4	16	6.0	1.9	68.4
Avg HRT=4	-	4	52	19.4	0.65	94.4
10 Jan	2	2	234	44.0	1.9	95.6
18 Jan	10	2	117	22.0	0.0	100.0
19 Jan	11	2	67	12.5	0.0	100.0
21 Jan	13	2	128	24.0	0.11	99.5
29 Jan	21	2	53	10.0	0.2	98.0
4 Feb	27	2	39	7.3	0.0	100.0
6 Feb	29	2	192	36.0	0.64	98.2
7 Feb	30	2	160	30.0	0.64	97.9
7 Feb	30	2	178	33.5	0.60	98.2
7 Feb	30	2	181	34.0	0.12	99.6
8 Feb	31	2	202	38.0	0.06	99.8
11 Feb	34	2	181	34.0	0.52	98.5
12 Feb	35	2	213	40.0	-	-
13 Feb	36	2	319	60.0	0.35	99.4
18 Feb	41	2	184	34.5	0.47	98.6
19 Feb	42	2	165	31.0	0.02	99.9
Avg HRT=2	-	2	163	30.6	0.38	98.9

*Established by continuous flow monitoring at specific HRT.

Table VIII. Filter 2, Nitrate Nitrogen Removals at 4 and 1 Hour HRT's

Date	Days of Operation*	HRT (hr)	NO_3-N Loading Rate (g/cu m/day)	Influent Conc. (mg/l)	Effluent Conc. (mg/l)	NO_3-N Removed (%)
28 Nov	28	4	12	4.6	0.0	100.0
11 Dec	41	4	10	3.8	0.0	100.0
12 Dec	42	4	63	23.8	0.95	96.0
13 Dec	43	4	57	21.5	0.8	96.3
17 Dec	47	4	61	23.0	0.8	96.6
20 Dec	50	4	39	14.5	1.6	89.0
28 Dec	58	4	66	25.0	0.1	99.5
31 Dec	61	4	35	13.0	-	-
3 Jan	64	4	36	13.5	-	-
Avg HRT=4	-	4	42	15.9	1.68	96.8
10 Jan	2	1	122	11.5	1.3	88.7
18 Jan	10	1	330	31.0	0.0	100.0
19 Jan	11	1	-	-	-	-
21 Jan	13	1	-	-	-	-
29 Jan	21	1	170	16.0	0.82	94.8
4 Feb	27	1	50	4.7	0.15	96.8
6 Feb	29	1	341	32.0	0.21	99.3
7 Feb	30	1	320	30.0	0.67	97.7
7 Feb	30	1	373	35.0	0.33	99.0
7 Feb	30	1	426	40.0	0.12	99.7
8 Feb	31	1	304	29.0	0.06	99.8
11 Feb	34	1	266	25.0	0.49	98.0
12 Feb	35	1	133	12.5	-	-
13 Feb	36	1	735	69.0	0.29	99.6
18 Feb	41	1	277	26.0	0.33	98.7
19 Feb	42	1	266	25.0	0.18	99.4
Avg HRT=1	-	1	294	27.6	0.38	97.8

*Established by continuous flow monitoring at specific HRT.

rates and consistently produced effluents with greater than 90 percent nitrate removals.

An examination of Figures 5 and 6 shows that a trend in removal efficiency was developed by the filter in its response to loading changes. The percent removal tended to decrease following an increase in nitrate nitrogen loading. The percent removal then recovered to its previous level of near steady state efficiency. It can also be seen from these figures that during the last 30 days of the investigation, radical changes in the nitrate loading did not seem to affect a correspondingly radical change in the system's efficiency. Notice at the point where the HRT was changed from 4 hr to either 1 or 2 hr that after the initial decrease in efficiency, the percent removal returned to the same level.

The fluctuations in COD removals also closely followed the same pattern as exhibited by changes in nitrate nitrogen loading with sharp decreases coming immediately after loading changes or a decrease in the HRT. However, the dampening effect of time on the magnitude of the removal fluctuations was not exhibited with COD as it was with nitrate nitrogen.

An examination of Table IX for influent and effluent nitrogen does not show any specific tendency to variations when the loading was changed. However, it should be noted that there was no nitrogen present in either of the filtered

Table IX. Influent and Effluent Nitrogen*

Date	Days of Operation**	HRT (hr)	Filter 1 Influent (mg/l)	Filter 1 Effluent (mg/l)	Filter 2 Influent (mg/l)	Filter 2 Effluent (mg/l)
3 Nov	2	4	0	4.5	1.1	0.22
21 Nov	20	4	0.36	3.4	1.1	1.1
21 Jan	13	2,1	3.4	0	7.6	0
1 Feb	24	2,1	3.9	0	1.7	0
11 Feb	34	2,1	5.0	0.9	3.4	1.3
18 Feb	41	2	-	-	1.7	2.8
19 Feb***	42	2	-	-	0	0
20 Feb***	43	1	0	0	-	-

*Measured as total Kjeldahl nitrogen.
**As established by continuous flow monitoring at specific HRT.
***Filtered samples.

samples, which would indicate that the large variations in influent and effluent nitrogen concentrations were due to the concentration of solids in the samples.

Tables X and XI show the suspended solids data in the filter effluent and in 1 ft sections of the filters, respectively. No trend in SS discharge is discernable from effluent data. The large variations are possibly due to the fact that the solids concentration would build up to a point where a larger than usual concentration of suspended solids had to be forced out to make room for new growth. The values in Table XI where gathered at the termination of the study and show the high solids retention which typify the submerged filter. Note, the variation in solids concentration between the filters at the different HRT's. The solids concentrations in filter 2, at 1 hr HRT, are on the average 25 percent greater than those measured in filter 1 at 2 hr HRT. This value corresponds favorably to the difference of 18 percent in SRT for the two filters, 15.6 days for filter 1 and 19.0 days for filter 2.

Dissolved oxygen was a parameter which showed no trend in its variation with a decrease in HRT. It should be noted from Table XII that in most instances the filter environment was not anaerobic as evidenced by the D.O. in the effluent. This may be accounted for by the possibility of some oxygen absorption by the sample as it was being drawn.

2. Effluent Quality

The influent and effluent data obtained for various

Table X. Effluent Suspended Solids

Date	Days of Operation*	Filter 1 (mg/l)	Filter 2 (mg/l)
29 Jan	59	36	16
31 Jan	61	24	6
5 Feb	28	8	2
6 Feb	29	24	50
7 Feb	30	20	16
14 Feb	37	28	20
Avg	-	23	18

*As established by continuous flow monitoring at specific HRT.

Table XI. Biological Solids in One-Foot Sections of Submerged Filters

Filter Height* (ft)	Filter 1 SRT = 15.6 Days (mg/l)	Filter 2 SRT = 19.0 Days (mg/l)
0-1	10,120	12,250
1-2	4,260	5,940
2-3	1,420	2,100

*As measured from the filter base (influent end) metric conversion 1 ft = 0.3048m

Table XII. Influent and Effluent Dissolved Oxygen

Date	Days of Operation*	Filter 1 Influent (mg/l)	Filter 1 Effluent (mg/l)	Filter 2 Influent (mg/l)	Filter 2 Effluent (mg/l)
15 Dec	45	1.5	0.4	1.7	0.2
31 Dec	61	1.8	0.9	1.5	0.6
6 Jan	67	0.2	0.2	0.8	0.3
28 Jan	20	0.8	0.0	0.9	0.0
31 Jan	23	-	-	1.3	0.0
6 Feb	29	2.6	0.0	-	-
10 Feb	33	1.8	0.6	2.5	0.0
20 Feb	43	1.8	1.0	1.4	0.5
Avg	-	1.5	0.4	1.4	0.2

*As established by continuous flow monitoring at specific HRT.

parameters monitored are given in Tables IX through XII. The effluent characteristics for the denitrification of the synthetic waste are summarized in Table XIII as operating parameters for the submerged filters. The submerged filters provide good quality effluent considering COD, 15.6 mg/l, nitrate nitrogen, 0.78 mg/l, and suspended solids, 20 mg/l.

The effluent was normally a very clear liquid with some visible readily settable suspended solids. The effluent had an unoffensive odor which diminished as it was exposed to the atmosphere. At times, however, there was a hydrogen sulfide odor which was fairly strong. This usually occured at times of high COD influent concentration.

3. Effect of Filter Height

During periods of near steady state filter operation at 2 and 1 hr HRT's, samples were withdrawn from the units at various heights. The resulting profiles are shown in Figures 8 through 11. As is evidenced by Figures 8 and 9, the highest rate of nitrate nitrogen and COD conversion takes place in the lowest 6 in. (15.24 cm) of the filters for both HRT's. After the waste reaches approximately 12 in. (30.5 cm) the substrate utilization rate decreases to a point where the microorganisms then act to provide additional conversions on the remaining original substrate and subsequent metabolites. (Figure 8)

Notice in Figure 8 the shape of the nitrite curve. Nitrite was present in the influent in only trace amounts,

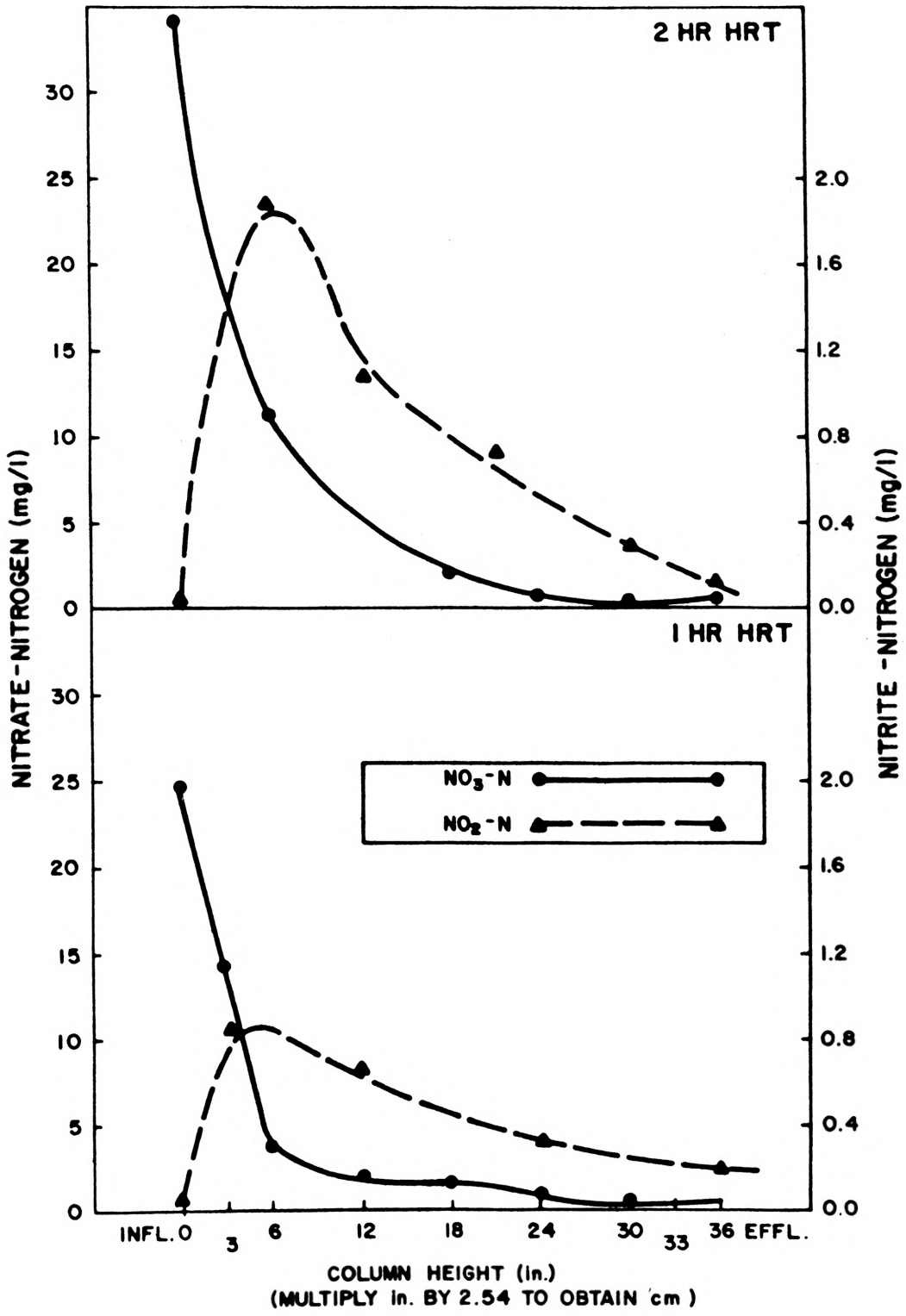


FIGURE 8. PROFILES OF NO_3-N AND NO_2-N CONCENTRATIONS

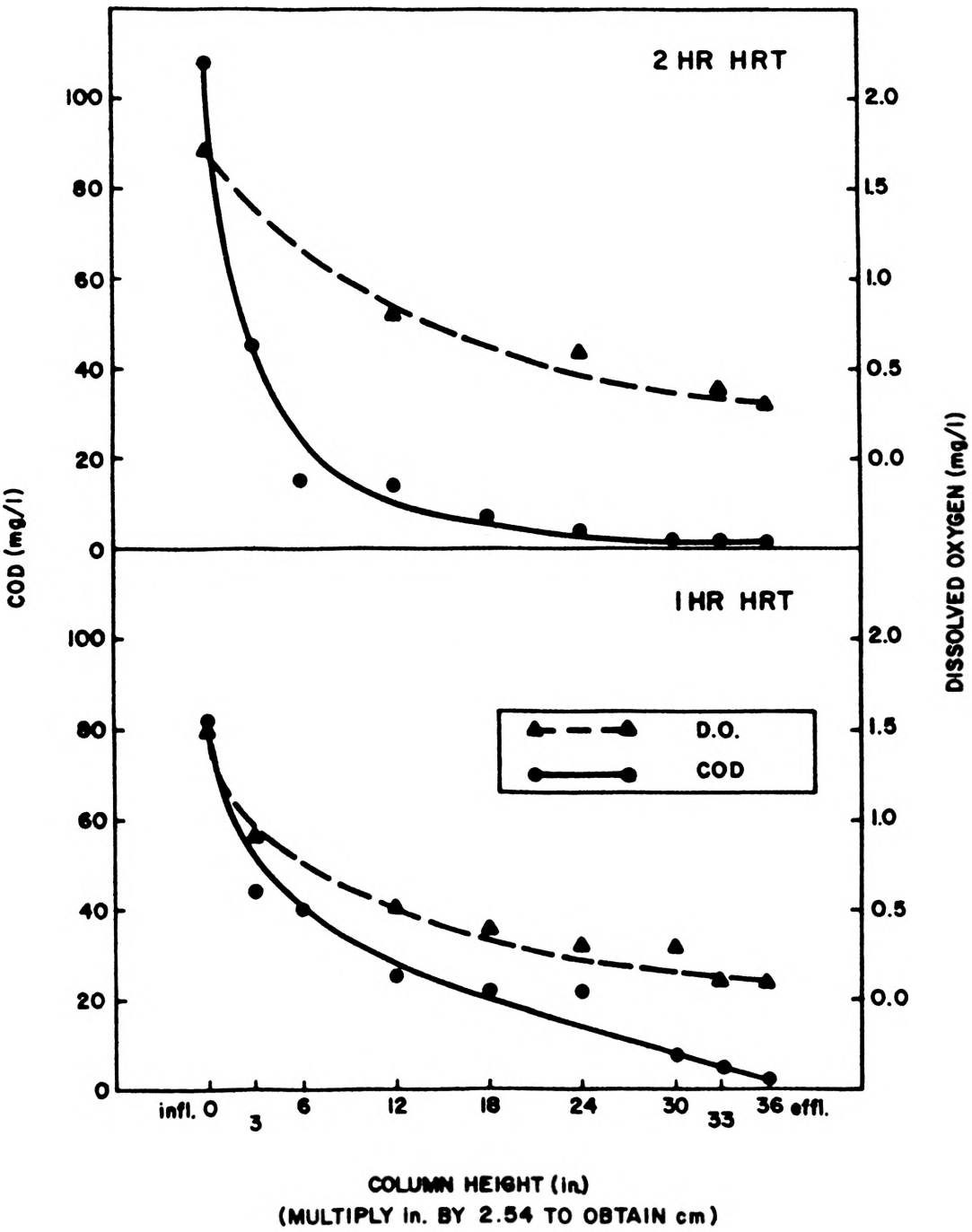


FIGURE 9. PROFILES OF COD CONCENTRATION AND DISSOLVED OXYGEN CONCENTRATION

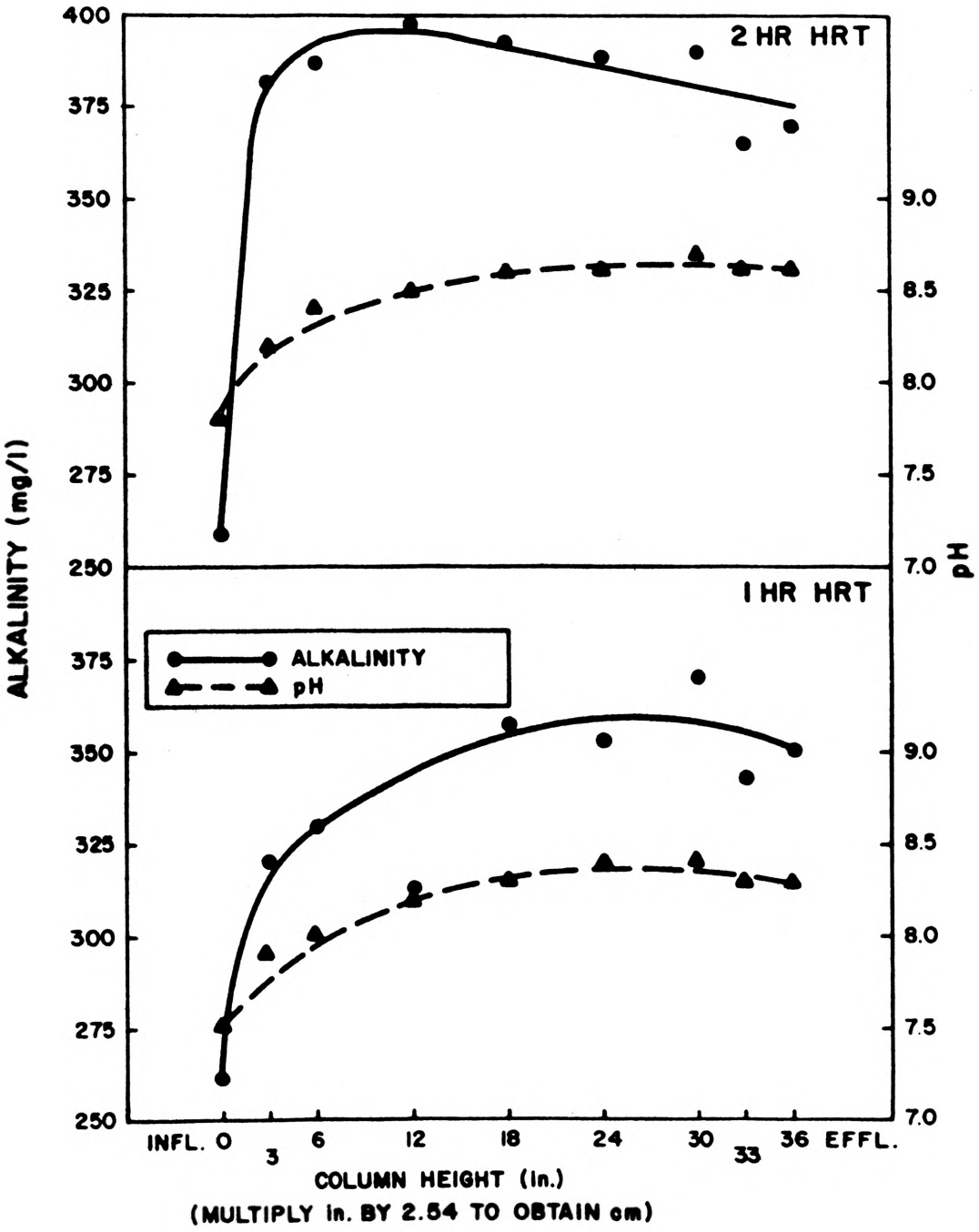


FIGURE 10. PROFILES OF ALKALINITY AND pH

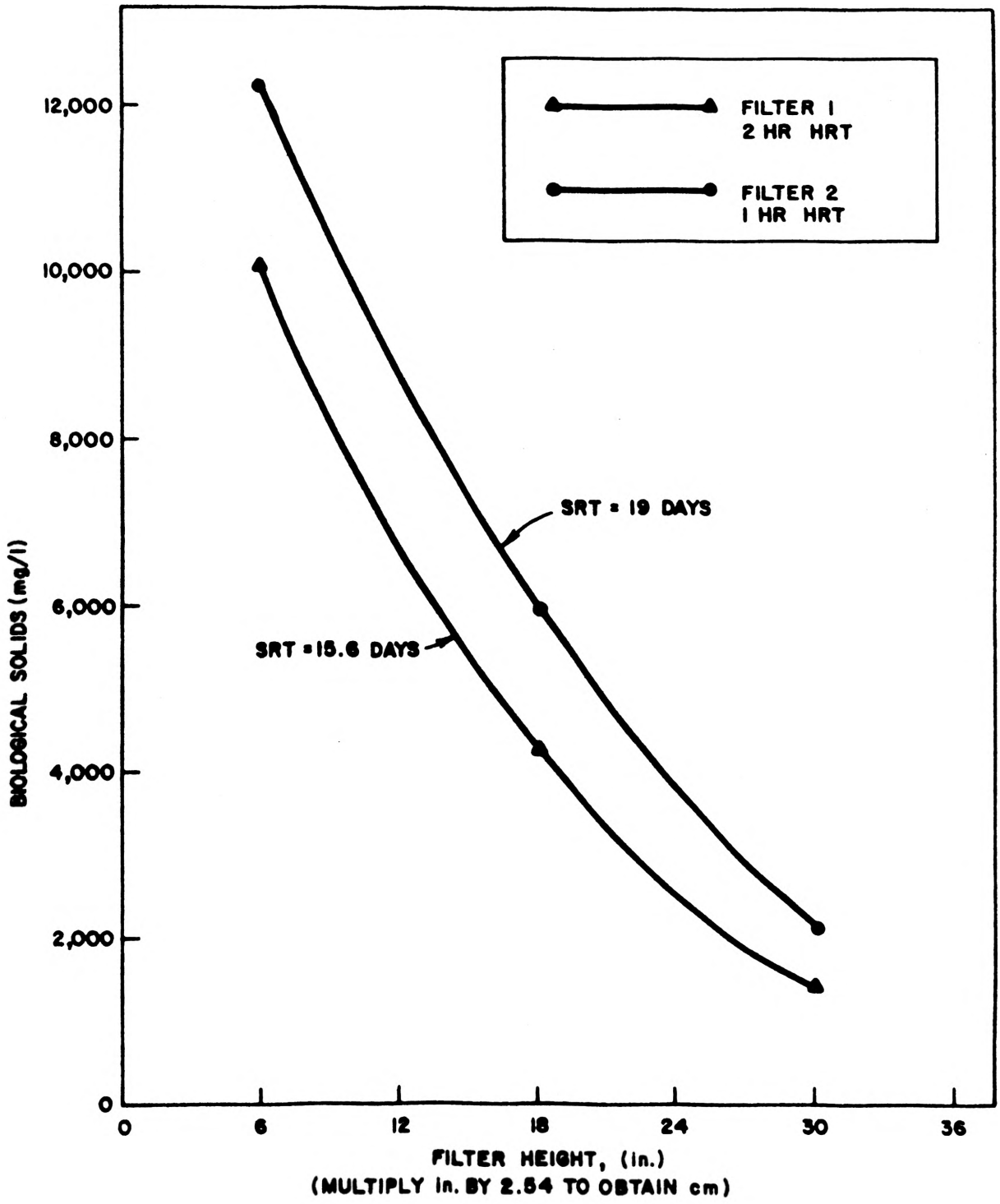


FIGURE 11. BIOLOGICAL SOLIDS vs. FILTER HEIGHT

yet the concentration rose to several mg/l within the filter, before declining again to a negligible quantity in the effluent. This formation and reduction of nitrite within the system tends to show the two-step denitrification process. The utilization of dissolved oxygen closely parallels that of nitrate and COD indicating that it was also removed most efficiently in the lower portion of the filters.

The overall increase of pH and alkalinity shown in Figure 10 is probably indicative of the hydroxyl ions released when nitrate nitrogen is reduced to gaseous nitrogen as shown by the summary equation for denitrifcation. (Eq. 8)

Figure 11 shows the biological solids concentrations of the filters. The biological solids were determined on one-foot sections of the filters and plotted at the midpoint of each section. At the termination of the study the filters were dismantled and the biological solids which had accumulated in the filter were recovered. As is evidenced by Figure 11, the high concentrations of solids in the lower portion of the filter corresponds to the high substrate utilization rates for nitrate and COD shown in Figures 8 and 9.

V. DISCUSSION

The primary objectives of this experimental study were to evaluate the performance of the facultative submerged filter for denitrification of a synthetic waste and to evaluate the kinetic equations which typify the biological denitrification process. In order to accomplish this aim the experimental results obtained had to be interpreted relative to the adequacy of the filter design, and the performance parameters monitored.

A. EXPERIMENTAL DESIGN

The selection of 1 to 1.5 in. (2.54-3.81 cm) stone and 6 in. (15.24 cm) diameter column was based on the results of previous studies of the submerged filters. (3), (6), (29) The major concern in a reactor of this type is that the combination of media size and reactor diameter would minimize geometric distortion of the filter performance. The combination chosen apparently fulfilled this objective. A significant problem has been encountered by other investigators with much smaller media in that plugging of the void spaces may occur and a regular cycle of flushing must be employed to prevent excessive head loss through the filter. (3), (31) In two instances, the filters used in this study became plugged so that a surge of water had to be employed to dislodge the biological growth. Both instances occured after periods of organic shock loading. A problem associated with larger aggregate

is that severe channeling or short circuiting may result, thus lowering the effective retention time and subsequently the filter efficiency.

The design of the feed system seemed to be adequate after certain modifications were made. Breakdown of the substrate concentrations resulted when the feed reservoirs were maintained at 35°C. This was remedied by keeping the feed solutions at room temperature, 20°C. Losses of substrate concentration through slime accumulation and subsequent increase of head loss through the feed lines was corrected by periodic acid cleaning and water rinsing. The major problem associated with the feed system was the eventual deterioration of the tubing walls by the mechanical action of the pumps. The tubing in these critical areas were replaced at intervals of one week or less as needed.

The dispersion plate in the base of the filters (see Figure 4) provided an effective means for distributing the waste across the bottom of the filter. The dispersion rings placed at one ft intervals appeared to be effective in preventing solids transfer and short circuiting through the large void spaces at the media-reactor interface. (29)

Biological solids became attached to the inside walls of the filter and the dispersion rings as well as to the media. Solids also filled the void spaces in the lower one-half of the filters. As previously mentioned, this solids accumulation became a problem in two instances when plugging occured. A possible solution would be a periodic

flushing of the reactor to force the biological growth higher into the filter, eventually to exit in the effluent. Another possibility would be a program of periodically resting one of a parallel battery of filters to allow a decrease in the number of microorganisms to naturally occur.

B. ANALYTICAL MEASUREMENTS

Throughout the study, the filter performance was evaluated by monitoring the effluent COD, nitrate nitrogen and nitrite nitrogen concentrations. The consistently high efficiencies experienced for nitrate removal, regardless of influent concentration, accomplished the stated objectives. The variability of the effluent COD concentrations, although normally low, illustrate that the addition of methanol as a carbon source must be closely monitored to prevent an excessive COD discharge from the reactor, or to prevent insufficient carbon from reaching the biological system. Nitrite nitrogen was monitored as a check on system efficiency and adequate methanol concentration. As can be seen from Figure 8, if insufficient COD is supplied, the two-step denitrification process may only proceed to partial completion, thus leaving a high residual nitrite concentration. This, in effect, may result in a further oxidation of the nitrite back to nitrate form, or a reduction to ammonia nitrogen upon discharge. In either case, the nitrogen contaminant remains in the effluent.

C. STEADY STATE OPERATION

Steady state operation of a wastewater treatment system implies several conditions. First, the influent flow rate, constituents and their concentrations are constant. Second, the effluent character is constant. Third, the concentration of any selected individual operational parameters at any point in the filter remains constant at that point for a prolonged period of time. In this study, although the hydraulic loading to the filters was constant over a period of time, the influent nitrate nitrogen concentration varied. Effluent nitrate nitrogen concentrations were relatively stable over a range of 0 to 1.0 mg/l. The concentrations of COD, D.O., nitrite nitrogen and nitrate nitrogen also fluctuated at the same point in the filters with respect to time. Therefore in the strictest sense of the word, steady-state conditions were not attained. However, steady-state conditions were assumed to exist when consistent percent removals of nitrate nitrogen were attained. A comparison of Figures 5 and 6 show that after a loading change, either substrate or hydraulic, both COD and nitrate removal efficiencies decreased for a time then returned to their prior values. It can also be noted that after about 15 days at an HRT equal to 1 hr, and after about 8 days at an HRT equal to 2 hr the nitrate removal efficiency did not vary by more than 3-5 percent for loading variations

of from 50 to 300 g/cu m/day. This would seem to support the capacity of the submerged filter to withstand quantitative substrate shock loads of large magnitudes. From observation of the curves for COD loading and efficiencies, the fluctuations of 20 to 30 percent in efficiency point out the need for an adequate methanol feed monitoring system for the denitrification process to minimize excess effluent COD.

The submerged filter is designed to utilize the long SRT's necessary to provide good anaerobic treatment. Observation of the solids retention characteristics of the filter indicated little or no correlation between effluent solids and treatment efficiencies. The fluctuations in the effluent suspended solids may have been the result of hydraulic changes, or sloughing of excess biological solids as is the case with trickling filters.

The effects of filter height on performance characteristics are illustrated in Figures 8, 9, and 11. The major portion of the substrate was removed in the lower portion of the filters. This can be accounted for by the fact that the lower portion of the filter contained the largest concentrations of biological solids (Figure 11). Microorganisms in the upper portions of the filter then act to provide additional conversions on the remaining original substrate and subsequent metabolites (Figure 8).

D. EVALUATION OF KINETIC EQUATIONS

The basic equations for biological denitrification

have been presented in the review of the literature. An evaluation of the submerged filter process as it compares to these equations follows.

The equations which describe the two-step process of denitrification (Eq. 6, 7, 8) are presented below with a comparison of the results obtained in this study.

First step: $NO_3^- + 1/3CH_3OH \rightarrow NO_2^- + 1/3CO_2 + 2/3H_2O$ {6}

The profiles shown in Figure 8 show nitrate and nitrite concentrations throughout the filter height and show a definite two-step reaction. The first step is essentially complete at the 6 in. height in filter 1 and the 3 in. height in filter 2. In filter 1 at 6 in., 23 mg/l of NO_3-N have been reduced while 24 mg/l of NO_2-N have been produced. In filter 2 at 3 in. 11 mg/l of NO_3-N have been reduced while 11 mg/l of NO_2-N have been produced.

Second step: $NO_2^- + 1/2CH_3OH \rightarrow 1/2N_2 + 1/2CO_2 + 1/2H_2O + OH^-$ {7}

Figure 8 also shows the nitrite nitrogen concentration having been reduced to near zero from the high levels reached at the completion of the first step. The summary reaction, the addition of steps one and two, also are verified. Notice that NO_2^- does not occur in Eq. 8 because it is formed and reduced within the system.

Summary: $NO_3^- + 5/6CH_3OH \rightarrow 1/2N_2 + 5/6CO_2 + 7/6H_2O + OH^-$ {8}

McCarty (18) presented the quantity of methanol required for denitrification (Eq. 12) and the synthesis of

biological solids (Eq 13).

$$Cm = 2.47N_o + 1.53N_1 + 0.87DO \quad \{12\}$$

The results obtained from this study of the submerged filter correlate satisfactorily with the methanol required for denitrification reported by McCarty in his batch and semi-continuous suspended growth studies.

$$C_b = 0.53N_o + 0.32N_1 + 0.19DO \quad \{13\}$$

Calculation of the biomass production by McCarty's equation and the results of this study also compare favorably. For filters 1 and 2 the calculated biomass production is equal to 17 and 15 mg/l respectively, while the actual concentrations of suspended solids were 23 and 18 mg/l for the submerged filter. It appears from these comparative results that the methanol required and the solids produced by the denitrification process is independent of the reactor type used, be it suspended growth or submerged filter.

E. SUMMARY OF FILTER PERFORMANCE

The starting procedure used for the submerged filter seemed satisfactory. Biological solids rapidly spread throughout the filter height from the initial 30 g of digester suspended solids which were seeded in the lower one-third of the filter. At the outset of the monitoring program on the continuous feed system, high removals for nitrate nitrogen were noted. Solids were not visible in the effluent.

The major portion of the initial substrate was removed

in the lower one-third of the filters at all hydraulic retention times. This can be accounted for by the fact that in the upflow submerged filter, the biological solids tend to settle into the void spaces at the bottom of the filter as well as the most favorable feed to microorganism ratio will exist in this region. Therefore, the highest rate of substrate utilization occurs in the area of the highest concentration of viable organisms. See Figure 11.

Definite trends were developed by the filter in its response to loading changes. The efficiency of both nitrate nitrogen and COD removals decreased subsequent to a change in hydraulic or substrate loading. Removal efficiencies were observed to return to prior levels following biological adjustments to the newly imposed conditions. In regards to nitrate nitrogen, however, the sudden losses of efficiency associated with loading changes and quantitative substrate shock loads decreased in magnitude toward the end of the study.

A summary of the loading and effluent characteristics for the three HRT's investigated is presented in Table XIV. Filter performance as based on nitrate nitrogen removal was excellent. Filter performance based on COD removal appeared to be affected by influent COD concentration. This lack of consistent removal efficiency for COD could be remedied by providing a monitoring and feed system that would meter

Table XIII. Operating Parameters for Submerged Filters at 4, 2 and 1 Hour HRT

Parameter*	Filter 1		Filter 2	
HRT (hr)	4	2	4	1
SRT (days)	-	15.6	-	19.0
COD Loading g/cu m/day	234	638	272	1169
COD Removal (percent)	79.4	91.4	90.0	86.0
NO_3 Loading g/cu m/day	52	163	42	294
NO_3 Removal (percent)	94.4	98.9	96.8	97.8
Effluent S.S. (mg/l)	-	23.0	-	18.0
Effluent D.O. (mg/l)	0.6	0.4	0.4	0.2
Effluent Nitrogen (mg/l)	0.0	0.0	0.0	0.0
Effluent NO_2-N (mg/l)	-	0.1	-	0.2
Effluent Alkalinity (mg/l)	-	375	-	350
Effluent pH (units)	8.4	8.6	8.2	8.3

*Average values

Table XIV. Summary of Filter Performance Under Varied Hydraulic Loadings

Parameter*	Hydraulic Retention Time (hr)		
	4	2	1
NO_3-N Loading (g/cu m/day)	47	163	294
Influent NO_3-N (mg/l)	18.0	31.0	28.0
Effluent NO_3-N (mg/l)	1.2	0.38	0.38
NO_3-N Removal (percent)	95.6	98.9	97.8
COD Loading (g/cu m/day)	253	638	1169
Influent COD (mg/l)	95	120	110
Effluent COD (mg/l)	15	14	17
COD Removal (percent)	85.0	91.3	86.0
Effluent NO_2-N (mg/l)	-	0.1	0.2
Effluent pH	8.3	8.6	8.3
Effluent Alkalinity (mg/l) as $CaCO_3$	-	375	350
Effluent Dissolved Oxygen	0.5	0.4	0.2
Effluent Suspended Solids	-	23.0	18.0
SRT (days)	-	15.6	19.0

*Average values

the required methanol based on influent nitrate nitrogen and dissolved oxygen concentrations.

In summary, the facultative submerged filter compares favorably to other denitrification processes with respect to loads which can be applied and the removals which can be attained. For the nitrate loading range of 9-735 g NO_3-N/cu m/day removals ranged from 95.6-98.9 percent. However, one of the most important factors when comparing the submerged filter to other denitrification processes is the fact that because of the solids retention characteristics of the filter, the low cellular synthesis rates and long solids retention times necessary to efficiently treat a high nitrate waste can be exploited without the need for solids wasting or recycle.

VI. CONCLUSIONS

The following conclusions are drawn for the performance of the facultative submerged filter, as determined by this investigation.

1) The submerged filter successfully treated a synthetic waste with nitrate nitrogen concentrations which ranged from 5 to 70 mg/l when operated at 35°C with removal efficiencies of 96.8 to 98.9 percent.
2) High treatment efficiencies were maintained without solids recycle when operated over a nitrate loading range of 9-735 g/cu m/day and a COD loading range of 178-2300 g/cu m/day.
3) Shock increases in organic and nitrate loadings did not result in failure of the submerged filter to treat the waste.
4) An evaluation of the kinetic equations for denitrification proved to be valid for the submerged filter.

VII. RESEARCH NEEDS FOR THE SUBMERGED FILTER

Based on the findings of this study the following topics are suggested for future investigations of the facultative submerged filter process.

1) An investigation of the various geometric parameters which might affect the performance of the submerged filter, to include column diameter and height, filter porosity, and media type and size.
2) A study of filter performance under ambient temperature variations.
3) An investigation of the effects of shock loadings and periodic resting of the filter.
4) An investigation of a methanol feed and monitoring system which meters the methanol in the correct proportion to nitrate nitrogen and dissolved oxygen present in the influent.

REFERENCES

1. Nogaj, R.J., "Removing Nitrogen from Wastewater Processes," Pollution Engineering, (October 1973).

2. McCarty, P. L., "Feasibility of the Denitrification Process for Removal of NO_3-N from Agricultural Drainage Waters," Appendix Calif. Dept. of Water Resources Bull. 174-3, (1969).

3. Tamblyn, T. A., and Sword, B. R., "The Anaerobic Filter for the Denitrification of Agricultural Subsurface Drainage," Proc. 25th Ind. Waste Conf., Purdue Univ. Ext. Ser. 130, 1135, (1969).

4. Slechta, A. F., and Culp, G. L., "Water Reclamation Studies of the South Tahoe Public Utility District," JWPCF 39, 787, (1967).

5. English, J. H., Carry, C. W., Masse, A. N., Pitkin, J. B., and Dryden, F.D., "Denitrification in Granular Carbon and Sand Columns", JWPCF 46, 1, (1974).

6. Young, J. C., and McCarty, P. L., "The Anaerobic Filter for Waste Treatment," JWPCF 41, Research Supp., R160, (1969).

7. Plummer Jr., A. H., Malina Jr., J. F., and Eckenfelder Jr., W. W., "Stabilization of a Low Solids Carbohydrate Waste by an Anaerobic Submerged Filter," Proc. 23rd Ind. Waste Conf., Purdue Univ., Ext. Ser. 132, 462, (1968).

8. Stensel, H. D., Loehr, R. C., and Lawrence, A. W., "Biological Kinetics of Suspended-growth Denitrification," JWPCF 45, 249, (1973).

9. Seidel, D. F., and Crites, R. W., "Evaluation of Anaerobic Denitrification Processes," Journ. San. Eng. Div., ASCE, 96, SA2, 267, (1970).

10. Jennett, J. C., and Dennis, N. D., Jr., "Anaerobic Filter Treatment of Pharmaceutical Waste," JWPCF, 47, 1, (1975).

11. Metcalf and Eddy, Wastewater Engineering, McGraw-Hill, New York, N. Y., (1972).

12. U.S. EPA Technology Transfer Publication, Nitrification and Denitrification Facilities Wastewater Facilities, PB 213-783, (Aug. 1973).

13. Eckenfelder, W. W., "Performance of a High Rate Trickling Filter Using Selected Media," JWPCF, 35, 12, (1963).

14. U.S. EPA Environmental Protection Technology Series, Application of Plastic Media Trickling Filters for Biological Nitrification Systems, EPA-R2-73-199, (June 1973).

15. Chipperfield, P.N.J., "Performance of Plastic Filter Media in Industrial and Domestic Waste Treatment," JWPCF, 34, 11, (1967).

16. Wilson, T. E., and Riddell, M.D.R., "Ammonia Nitrogen Control Methods." Paper presented at the Thirty-Eighth Annual Water Pollution Control Operator Conference, Springfield, Illinois, (April 1973).

17. Culp, R. L., and Culp, G. L., Advanced Wastewater Treatment. Van Nostrand Reinhold Co., New York, N.Y., (1971).

18. McCarty, P. L., Beck, L., and St. Amant, P., "Biological Denitrification of Waste Waters by Addition of Organic Materials." Proc. 24th Ind. Waste Conf., Purdue Univ., Ext. Ser 135, 1271, (1969).

19. Requa, D. A., and Schroeder, E. D., "Kinetics of Packed-bed Denitrification." JWPCF 45, 1696, (1973).

20. Painter, H. A., "A Review of Literature on Inorganic Nitrogen Metabolism in Microorganisms." Water Research, 4, 393, (1970).

21. Schroeder, E. D., and Busch, A. W., "The Role of Nitrate Nitrogen in Bio-Oxidation." JWPCF 40, (1969).

22. Moore, S. E., and Schroeder, E. D., "An Investigation of the Effect of Residence Time on Anaerobic Bacterial Denitrification." Water Research, 4, 685, (1970).

23. Mulbarger, M. C., "The Three Sludge System for Nitrogen and Phosphorus Removal." EPA Tech. Transfer Seminar, PB-213-778, (April 1972).

24. Johnson, W. K., "Process Kinetics for Denitrification." Journ. San. Eng. Div., ASCE, 98, SA2, (1972).

25. Kugelman, I. J., "Status of Advanced Waste Treatment." EPA Tech. Transfer Seminar, PB-213-819, (May, 1972).

26. Cohen, J. M., "Nutrient Removal from Wastewater by Physical-Chemical Processes," EPA Tech. Transfer Seminar, PB-213-783, (March 1971).

27. Barth, E. F., Bremmer, R. C., and Lewis, C. F., "Chemical-Biological Control of Nitrogen and Phosphorus in Wastewater Effluent," JWPCF 40, 21, (1958).

28. Jeris, John S., Beer, Carl, and Mueller, James A., "High Rate Biological Denitrification Using a Granular Fluidized Bed." JWPCF 46, 9, (1974).

29. Dennis, Jr., D. D., Treatment of a Pharmaceutical Waste with the Anaerobic Filter. Thesis presented to the Graduate School of the University of Missouri-Rolla, (1973).

30. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Inc., (1970).

31. Sutton, P. M., Murphy, K. L., Dawson, R. N., "Low-Temperature Biological Denitrification of Wastewater." JWPCF 47, 1, (1975).

VITA

Dominic Joseph Grana was born on May 2, 1950, in St. Louis, Missouri, where he received his primary and secondary education. In September of 1968 he enrolled at the University of Missouri-Rolla, where he received the degree of Bachelor of Science in Civil Engineering in August 1972.

Upon graduation he enrolled at the University of Missouri-Rolla for graduate study. He is a student member of the American Society of Civil Engineers, the National Society of Professional Engineers, Chi Epsilon, and the Water Pollution Control Association.

Mr. Grana was married to Miss Rosemary Curran on January 8, 1972, and is the father of two children, Dominic Robert and Emily. He was commissioned as a Second Lieutenant in the United States Army on July 29, 1972.

Currently, Mr. Grana holds a position in the Engineering Operations Department of Ryckman, Edgerley, Tomlinson and Associates, Inc., St. Louis, Missouri, as an Environmental Engineer.